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16. ABSTRACT

The report gives results of an analysis of atmospheric (air) emissions from ortho-xylene- and naphthalene-based phthalic anhydride manufacturing plants. Uncontrolled and controlled emission factors are given for each species emitted to the atmosphere from each source within a typical plant, based on the latest data available. Emissions data are used to calculate three factors designed to quantify the hazard potential of the emissions: (1) source severity (the ratio of maximum mean ground-level concentration of a pollutant to the concentration which constitutes an incipient health hazard), (2) the industry contribution to total atmospheric emissions of criteria pollutants, and (3) the population exposed to high contaminant levels from a representative plant. Detailed process descriptions and flow sheets are presented for the BASF fixed-bed ortho-xylene process and the Badger-Sherwin-Williams fluid-bed naphthalene process. Present and future aspects of pollution control technology in the industry are discussed, including a number of possible process modifications. Economic and production trends in the phthalic anhydride industry and in each of the industries that are major consumers of phthalic anhydride are analyzed. Water-related emissions are to be discussed in a future, separate report.

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SOURCE ASSESSMENT:
PHTHALIC ANHYDRIDE
(AIR EMISSIONS)

by

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Prepared for

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Washington, DC 20460

PREFACE

The Industrial Environmental Research Laboratory (IERL) of EPA has the responsibility for insuring that pollution control technology is available for stationary sources to meet the requirements of the Clean Air Act, the Water Act and the Solid Waste legislation. If control technology is unavailable, inadequate, uneconomical or socially unacceptable, then financial support is provided for the development of the needed control techniques for industrial and extractive process industries. Approaches considered include: process modifications, feedstock modifications, add-on control devices, and complete process substitution. The scale of the control technology programs ranges from bench to full scale demonstration plants.

The Chemical Processes Branch of the Industrial Processes Division of IERL has the responsibility for investing tax dollars in programs to develop control technology for a large number (>500) of operations in the chemical industries. As in any technical program, the first question to answer is, "Where are the unsolved problems?" This is a determination which should not be made on superficial information; consequently, each of the industries is being evaluated in detail to determine if there is, in EPA's judgment, sufficient environmental risk associated with the process to invest in the development of control technology. This report contains the data necessary to make that decision for the air emissions from phthalic anhydride manufacture.

Monsanto Research Corporation has contracted with EPA to investigate the environmental impact of various industries which represent sources of pollution in accordance with EPA's responsibility as outlined above. Dr. Robert C. Binning serves as Program Manager in this overall program entitled, "Source Assessment," which includes the investigation of sources in each of four categories: combustion, organic materials, inorganic materials and open sources. In this study of phthalic anhydride manufacture, Mr. Kenneth L. Baker and Mr. Fdward J. Wooldridge served as EPA Project Leaders.

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LIST OF SYMBOLS

Symbol	Definition
A	Area
C	Diameter factor
Cap	Production capacity
C_i	Production capacity of plant i
D	Tank diameter
$\overline{D}_p$	Mean population density
D_{p_i}	County population density for plant i
e	2.72
E	Emission factor, g/kg
E'	Emission factor, lb/ton
F	Hazard factor
F_g	Equivalent gasoline working loss
F_p	Paint factor
H	Effective emission height
H'	Tank outage
K_T	Turnover factor
L	Total petrochemical loss, barrels
L_1	Total petrochemical loss, pounds
L_g	Total equivalent gasoline loss
L_y	Equivalent gasoline breathing loss
M	Molecular weight
N	Number of turnovers per year
P	Vapor pressure
Q	Mass emission rate
S	Source severity
t, t_0	Averaging times
$\overline{u}$	Average wind speed
V	Tank capacity
W	Liquid density

LIST OF SYMBOLS (continued)

Symbol	Definition
x	Distance downwind from source
ΔT	Average daily ambient temperature change
σ_z	Vertical dispersion coefficient
χ_{max}	Maximum mean ground level concentration (short term average)
$\bar{\chi}_{max}$	Maximum mean ground level concentration (long-term average)
$\bar{\chi}(x)$	Annual mean ground level concentration

SECTION I

INTRODUCTION

Phthalic anhydride (PAN) is an important industrial chemical which is principally used in the manufacture of plasticizers, polyester resins, and alkyd resins. Present production capacity in the United States is nearly 5 x 10^5 metric tons/yr.[a] Phthalic anhydride is manufactured by the catalytic vapor-phase oxidation of either *ortho*-xylene (designated herein as o-xylene) or naphthalene. The o-xylene based plants employ fixed-bed reactors, while the naphthalene based plants use the fluid-bed process. This document presents a detailed study of the phthalic anhydride industry from the standpoint of atmospheric emissions and their potential environmental impact.

The major results of this study, summarized in Section II, include emission factors for each species emitted to the atmosphere from each emission point within a representative phthalic anhydride plant. Also tabulated are several factors designed to measure the environmental hazard potential of phthalic anhydride operations. These include source severity factors, the industry contribution to total atmospheric emissions of criteria pollutants, and the population affected by a representative plant.

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[a] 1 metric ton = 10^6 grams = 2205 pounds = 1.1 short tons (short tons are designated "tons" in this document); other conversion factors and metric system prefixes are presented in Section IX.

Detailed descriptions of phthalic anhydride manufacturing processes are given in Section III. Discussion is limited to the BASF (Badische Anilin und Soda-Fabrik) process for the oxidation of o-xylene, and the Badger-Sherwin-Williams process for the oxidation of naphthalene, since these two processes dominate the industry. Included are descriptions of each major processing step, flow diagrams, process chemistry, and material and energy balances.

Atmospheric emissions from phthalic anhydride plants are discussed in Section IV. The species known to be emitted and/or produced by the processes are detailed, and each emission point within the plant is described. Compositions and flow rates of streams emitted to the atmosphere are provided. A representative phthalic anhydride plant is defined, and emission factors for such a plant employing the best available control technology are given. These emission factors are then used to generate source severity factors, the industry contribution to total emissions of criteria pollutants, and the affected population.

Present and future aspects of pollution control technology in the phthalic anhydride industry are considered in Section V. Several process modifications are described which are likely to have an impact upon the industry in the near future.

Economic and production trends in the phthalic anhydride industry are addressed in Section VI. The trends in each of the industries that are major consumers of phthalic anhydride are also analyzed. Finally, estimates of phthalic anhydride production through the remainder of the present decade are discussed.

SECTION II

SUMMARY

Phthalic anhydride is manufactured by the catalytic vapor-phase oxidation of either o-xylene or naphthalene. There are currently 10 phthalic anhydride plants operating in the continental United States, plus one in Puerto Rico, having a total capacity of 4.95 x 10^5 metric tons/yr (5.44 x 10^5 tons/yr). Of the plants in the continental U.S., seven utilize o-xylene as a feedstock and the remaining three use naphthalene. All of the o-xylene based plants employ fixed-bed reactors, while the three naphthalene based plants use fluid-bed processes. The population densities of the counties in which the plants are located range from 30 to 4,905 persons per square kilometer.

Sources of atmospheric emissions within phthalic anhydride plants include the scrubber vent(s) and/or incinerator stack(s), storage tanks, the flaker and bagger vents, the transport loading facility vent, and fugitive emissions. The catalyst storage hopper vents are additional sources of emissions in naphthalene based plants.

The main process waste gas from the phthalic anhydride switch condensers is controlled either by a scrubber-incinerator combination or by direct incineration. The latter method has the advantage of providing control of carbon monoxide as well as the organic species in the waste gas. Either the scrubber or the incinerator, or both, may also be used to control the waste streams from the product purification section of the plant. Alternatively, a separate scrubber or incinerator may be used to control these streams.

Storage tanks contain o-xylene or naphthalene, crude phthalic anhydride, and refined phthalic anhydride. Available control devices include conservation vents on o-xylene and naphthalene tanks, and condensers or sublimation traps on phthalic anhydride tanks. The latter tanks may also be vented to the incinerator for control.

In the flaking and bagging operations, liquid phthalic anhydride is solidified in the form of flakes and packaged in bags for shipment. The vents from these operations are ducted to a cyclone and/or a baghouse for control. Phthalic anhydride is also shipped in the liquid form. At the transport loading facility, liquid phthalic anhydride is pumped into tank trucks or railway tank cars for shipment.

Fugitive emissions include heat-transfer oil (e.g., Dowtherm A®, a diphenyl-diphenyl oxide eutectic mixture) which escapes from the heat-transfer circuits during process upsets. In the case of naphthalene based plants, vanadium oxide catalyst dust is also emitted during catalyst transfer operations in which the fluid-bed catalyst is pneumatically conveyed between the storage hoppers and the reactor. Vents on the catalyst storage hoppers are additional sources of emissions during these operations. The vents are equipped with cyclone separators for emissions control.

Emissions data for o-xylene based plants are summarized in Table 1. The data correspond to a plant with a dual incineration control system, which represents the best available control technology. The main process incinerator controls

Table 1. SUMMARY OF EMISSION DATA FOR A REPRESENTATIVE o-XYLENE BASED PHTHALIC ANHYDRIDE PLANT

Species emitted	Emission factor,[a] g/kg		Control efficiency, %
	Uncontrolled	Controlled	
Particulate			
Main process incinerator	-[b]	0.25 ± 50%	-
Secondary incinerator	-[b]	0.125 ± 50%	-
Flaker and bagger	0.10	0.001	99
Sulfur oxides			
Main process incinerator	5.0 ± 25%	5.0 ± 25%	0
Nitrogen oxides			
Main process incinerator	-[c]	1.25 ± 50%	-
Secondary incinerator	-[c]	0.125 ± 25%	-
Carbon monoxide			
Main process incinerator	125.0 ± 20%	0.125 ± 50%	99.9
Secondary incinerator	-[c]	1.25 ± 50%	-
Maleic anhydride			
Main process incinerator	52.0 ± 20%	1.82 ± 25%	96.5
Secondary incinerator	3.75 ± 83%	0.038 ± 90%	99
Phthalic anhydride			
Main process incinerator	15.6 ± 20%	0.545 ± 25%	96.5
Secondary incinerator	10.6 ± 53%	0.106 ± 60%	99
Storage tanks	0.29 ± 10%	0.003 ± 20%	99
Flaker and bagger	0.10	0.001	99
Transport loading	0.45 ± 10%	0.005 ± 20%	99
Fugitive emissions	-[b]	-[d]	
Benzoic acid			
Main process incinerator	3.12 ± 20%	0.109 ± 25%	96.5
Secondary incinerator	1.25 ± 50%	0.0125 ± 55%	99
Diphenyl oxide[e]			
Fugitive emissions	0.016	-[d]	-
o-Xylene			
Storage tanks	0.20 ± 10%	0.002 ± 20%	99
Formaldehyde			
Main process incinerator	2.1[f]	0.074[f]	96.5
Secondary incinerator	-[b]		
Total hydrocarbons[g]			
Main process incinerator	72.8 ± 30%	2.6 ± 30%	96.5
Secondary incinerator	18.8 ± 60%	0.16 ± 60%	99
Storage tanks	0.49 ± 10%	0.005 ± 20%	99
Flaker and bagger	0.1	0.001	99
Transport loading	0.45 ± 10%	0.005 ± 20%	99
Fugitive emissions	0.116	-[d]	-

[a] Emission factor is defined as weight of emission per unit weight of phthalic anhydride product.

[b] Emission data not available.

[c] No emissions generated in uncontrolled process.

[d] Fugitive emissions are not controlled.

[e] Heat-transfer fluid, assumed to be Dowtherm A.

[f] Total aldehydes reported as formaldehyde.

[g] Includes all non-methane organic species.

the main process waste gas and the secondary incinerator handles the waste streams from the product purification section of the plant. Error bounds on the emission factors were estimated wherever possible.

Emissions data for a naphthalene based plant with a dual incineration control system are presented in Table 2. In arriving at these values it was assumed that this control system, which is currently in operation on an o-xylene based plant, could be applied to a naphthalene based plant without altering the control efficiency of the system. The accuracy of the emission factors in Table 2 is believed to be generally poorer than that of the values listed in Table 1, as reflected in the estimated error bounds.

In order to quantify the hazard potential of phthalic anhydride operations, a severity factor was defined which represents the ratio of the mean maximum ground level exposure to the hazard level of exposure for a given pollutant from a given source. Using Gaussian plume dispersion theory together with the controlled emission factors in Tables 1 and 2, severity factors were calculated for o-xylene and naphthalene based plants having production capacities of 5.9 x 10^4 metric tons/ yr (6.5 x 10^4 tons/yr). The results are summarized in Tables 3 and 4. Also listed are the annual mass emissions from a single plant and from the phthalic anhydride industry, and the percentage contribution of the industry to the total mass emissions of criteria pollutants (particulate, NO_x, SO_x, CO, and hydrocarbons). These values are all based on the controlled emission factors listed in Tables 1 and 2, and, hence, represent hypothetical emissions which would occur if all plants employed the best available control technology.

Table 2. SUMMARY OF EMISSION DATA FOR A REPRESENTATIVE NAPHTHALENE BASED PHTHALIC ANHYDRIDE PLANT

Species emitted	Emission factor,[a] g/kg		Control efficiency, %
	Uncontrolled	Controlled	
Particulate			
Main process incinerator	-[b]	0.25 ± 70%	-
Secondary incinerator	-[b]	0.125 ± 70%	-
Flaker and bagger	0.10	0.001	99
Nitrogen oxides			
Main process incinerator	-[c]	1.25 ± 70%	-
Secondary incinerator	-[c]	0.125 ± 40%	-
Carbon monoxide			
Main process incinerator	50.5 ± 50%	0.05 ± 70%	99.9
Secondary incinerator	-[c]	1.25 ± 70%	-
Phthalic anhydride			
Main process incinerator	20.4 ± 40%	0.71 ± 50%	96.5
Secondary incinerator	9.8 ± 70%	0.10 ± 80%	99
Storage tanks	0.37 ± 10%	0.004 ± 20%	99
Flaker and bagger	0.10	0.001	99
Transport and loading	0.45	0.005	99
Fugitive emissions	-[b]	-[d]	
Maleic anhydride			
Main process incinerator	7.0 + 200%	0.24 + 200%	96.5
Secondary incinerator	4.9 ± 80%	0.05 ± 90%	99
Benzoic acid			
Main process incinerator	1.56 ± 40%	0.05 ± 50%	96.5
Secondary incinerator	-[b]	-[b]	
Naphthoquinone			
Main process incinerator	0.69 ± 40%	0.02 ± 50%	96.5
Secondary incinerator	6.6 ± 70%	0.07 ± 80%	99
Naphthalene			
Storage tanks	0.60 ± 10%	0.006 ± 20%	99
Vanadium oxide catalyst			
Catalyst storage	0.41	0.01	97.5
Fugitive emissions	-[b]	-[d]	
Diphenyl oxide[e]			
Fugitive emissions	0.016	-[d]	-
Formaldehyde			
Main process incinerator	2.1[f]	0.074[f]	96.5
Secondary incinerator	-[b]	-[b]	
Total hydrocarbons[g]			
Main process incinerator	31.8 + 79% - 35%	1.09 + 85% - 40%	96.5
Secondary incinerator	26.5 ± 70%	0.27 ± 80%	99
Storage tanks	0.97 ± 10%	0.01 ± 20%	99
Flaker and bagger	0.1	0.001	99
Transport loading	0.45 ± 10%	0.005 ± 20%	99
Fugitive emissions	0.116	-[d]	-

[a] Emission factor is defined as weight of emission per unit weight of phthalic anhydride product.

[b] Emission data not available.

[c] No emissions generated in uncontrolled process.

[d] Fugitive emissions are not controlled.

[e] Heat-transfer fluid, assumed to be Dowtherm A.

[f] Total aldehydes reported as formaldehyde.

[g] Includes all non-methane organic species.

Table 3. SOURCE SEVERITY FACTORS AND INDUSTRY CONTRIBUTION TO TOTAL EMISSIONS FOR o-XYLENE BASED PHTHALIC ANHYDRIDE PRODUCTION (CONTROLLED EMISSIONS)

Species emitted	Emissions from all plants,[a] metric tons/yr	Emissions from representative plant,[b] metric tons/yr	Severity factor,	Industry contribution to total emissions,[c] %					
				Nationwide	California	Illinois	Louisiana	New Jersey	Texas
Particulate (total)	113	22.2		0.00063	0.0014	0.0033	0.0039	0.0148	0.0040
Main process incinerator		14.8	0.0095						
Secondary incinerator		7.4	0.019						
Flaker and bagger		0.06	0.0038						
Sulfur oxides (total)	1,500	295.0		0.0050	0.0492	0.0249	0.1200	0.0641	0.0393
Main process incinerator		295.0	0.14						
Nitrogen oxides (total)	413	81.2		0.0018	0.0032	0.0144	0.0133	0.0166	0.0062
Main process incinerator		73.8	0.14						
Secondary incinerator		7.4	0.061						
Total hydrocarbons[d] (total)	865	170.3		0.0034	0.0051	0.0161	0.0061	0.0208	0.0077
Main process incinerator		153.4	0.23						
Secondary incinerator		9.4	0.056						
Storage tanks		0.30	0.0071						
Flaker and bagger		0.06	0.0088						
Transport loading		0.30	0.044						
Fugitive emissions		6.8	4.0						
Carbon monoxide (total)	413	81.2		0.00042	0.0006	0.0022	0.0010	0.0028	0.0012
Main process incinerator		7.4	0.000053						
Secondary incinerator		73.8	0.0021						
Phthalic anhydride (total)	198	39.0							
Main process incinerator		32.2	0.28						
Secondary incinerator		6.3	0.20						
Storage tanks		0.18	0.024						
Flaker and bagger		0.06	0.050						
Transport loading		0.30	0.24						
Fugitive emissions									
Maleic anhydride (total)	557	109.6							
Main process incinerator		107.4	5.4						
Secondary incinerator		2.2	0.45						

[a] Emissions not calculated for individual emission points.

[b] A representative plant is defined to be one having a production capacity of 5.9×10^4 metric tons/yr (6.5×10^4 tons/yr)

[c] Industry contribution calculated only for criteria pollutants.

[d] Includes all non-methane organic species.

Table 3 (continued). SOURCE SEVERITY FACTORS AND INDUSTRY CONTRIBUTION TO TOTAL EMISSIONS FOR o-XYLENE BASED PHTHALIC ANHYDRIDE PRODUCTION (CONTROLLED EMISSIONS)

Species emitted	Emissions from all plants,[a] metric tons/yr	Emissions from representative plant,[b] metric tons/yr	Severity factor,	Industry contribution to total emissions,[c] %					
				Nationwide	California	Illinois	Louisiana	New Jersey	Texas
Benzoic acid (total)	36	7.1							
Main process incinerator		6.4	0.0065						
Secondary incinerator		0.74	0.0030						
Diphenyl oxide[e] (total)	4.8	0.94							
Fugitive emissions		0.94	18.5						
o-Xylene (total)	0.6	0.12							
Storage tanks		0.12	0.00022						
Formaldehyde (total)	22	4.4[f]							
Main process incinerator		4.4[f]	0.074[f]						
Secondary incinerator		-[g]	-[g]						

[a] Emissions not calculated for individual emission points.

[b] A representative plant is defined to be one having a production capacity of 5.9 x 10^4 metric tons/yr (6.5 x 10^4 tons/yr)

[c] Industry contribution calculated only for criteria pollutants.

[e] Heat-transfer fluid, assumed to be Dowtherm A.

[f] Total aldehydes reported as formaldehyde.

[g] Data not available.

Table 4. SOURCE SEVERITY FACTORS AND INDUSTRY CONTRIBUTION TO TOTAL EMISSIONS FOR NAPHTHALENE BASED PHTHALIC ANHYDRIDE PRODUCTION (CONTROLLED EMISSIONS)

Species emitted	Emissions from all plants,[a] metric tons/yr	Emissions from representative plant,[b] metric tons/yr	Severity factor	Industry contribution to total emissions,[c] %		
				Nationwide	New Jersey	Pennsylvania
Particulate (total)	56	22.2		0.00031	0.0102	0.0023
Main process incinerator		14.8	0.0095			
Secondary incinerator		7.4	0.019			
Flaker and bagger		0.06	0.0038			
Nitrogen oxides (total)	206	81.2		0.0009	0.0114	0.0049
Main process incinerator		73.8	0.14			
Secondary incinerator		7.4	0.061			
Total hydrocarbons[d] (total)	224	88.1		0.0009	0.0074	0.0182
Main process incinerator		64.4	0.10			
Secondary incinerator		15.9	0.095			
Storage tanks		0.59	0.014			
Flaker and bagger		0.06	0.0088			
Transport loading		0.30	0.044			
Fugitive emissions		6.8	4.0			
Carbon monoxide (total)	195	76.8		0.00020	0.0018	0.0038
Main process incinerator		3.0	0.000021			
Secondary incinerator		73.8	0.0021			
Phthalic anhydride (total)	123	48.4				
Main process incinerator		41.9	0.36			
Secondary incinerator		5.9	0.20			
Storage tanks		0.24	0.032			
Flaker and bagger		0.06	0.050			
Transport loading		0.30	0.24			
Maleic anhydride (total)	44	17.2				
Main process incinerator		14.2	0.72			
Secondary incinerator		3.0	0.60			
Benzoic acid (total)	7.6	3.0				
Main process incinerator		3.0	0.0030			
Secondary incinerator		-[e]	-[e]			
Naphthoquinone (total)	13	5.3				
Main process incinerator		1.2	0.15			
Secondary incinerator		4.1	2.1			

[a] Emissions not calculated for individual emission points.

[b] Representative plant is defined to be one having a production capacity of 5.9×10^4 metric tons/yr (6.5×10^4 tons/yr)

[c] Industry contribution calculated only for criteria pollutants.

[d] Includes all non-methane organic species.

[e] Data not available.

Table 4 (continued). SOURCE SEVERITY FACTORS AND INDUSTRY CONTRIBUTION TO TOTAL EMISSIONS FOR NAPHTHALENE BASED PHTHALIC ANHYDRIDE PRODUCTION (CONTROLLED EMISSIONS)

Species emitted	Emissions from all plants,[a] metric tons/yr	Emissions from representative plant,[b] metric tons/yr	Severity factor	Industry contribution to total emissions,[c] %		
				Nationwide	New Jersey	Pennsylvania
Naphthalene (total)	0.9	0.35				
Storage tanks		0.35	0.0058			
Vanadium oxide catalyst (total)	1.5	0.59				
Catalyst storage		0.59	1.4			
Fugitive emissions						
Diphenyl oxide[f] (total)	2.4	0.94				
Fugitive emissions		0.94	18.5			
Formaldehyde (total)	11[g]	4.4[g]				
Incinerator I		4.4[g]	0.074[g]			
Incinerator II						

[a] Emissions not calculated for individual emission points.

[b] Representative plant is defined to be one having a production capacity of 5.9 x 10^4 metric tons/yr (6.5 x 10^4 tons/yr)

[c] Industry contribution calculated only for criteria pollutants.

[f] Heat-transfer fluid, assumed to be Dowtherm A.

[g] Total aldehydes reported as formaldehyde.

Phthalic anhydride production in 1973 totaled 4.658 x 10^5 metric tons (5.12 x 10^5 tons) in the United States. Production in 1978 is expected to total 4.99 x 10^5 metric tons (5.49 x 10^5 tons). Thus, assuming that the same level of control exists in 1978 as existed in 1973, emissions from the phthalic anhydride industry will increase by 7% over that period; i.e.:

$$\frac{\text{Emissions in 1978}}{\text{Emissions in 1973}} = \frac{4.99 \times 10^5}{4.658 \times 10^5} = 1.07$$

The average number of persons exposed to high contaminant levels from phthalic anhydride operations was estimated and designated as the "affected population." The calculation was made for each species emitted and for each emission point within a representative plant for which the severity factor exceeds 0.1 or 1.0. The results are presented in Table 5. The largest values of affected population are 525,000 persons for o-xylene based production and 9,200 persons for naphthalene based production.

Table 5. AFFECTED POPULATION
(number of persons)

Compound	o-Xylene based plant		Naphthalene based plant	
	No. of persons where $\overline{\chi}/F \geq 1.0$	No. of persons where $\overline{\chi}/F \geq 0.1$	No. of persons where $\overline{\chi}/F \geq 1.0$	No. of persons where $\overline{\chi}/F \geq 0.1$
Sulfur oxides				
Main process incinerator	0	6,700	–[a]	–[a]
Nitrogen oxides				
Main process incinerator	0	5,600	0	870
Total hydrocarbons				
Main process incinerator	0	9,600	0	0
Fugitive emissions	40	500	6	77
Phthalic anhydride				
Main process incinerator	0	19,000	0	4,100
Secondary incinerator	0	3,100	0	460
Transport loading	0	140	0	22
Maleic anhydride				
Main process incinerator	44,000	525,000	0	9,200
Secondary incinerator	0	8,800	0	1,800
Diphenyl oxide				
Fugitive emissions	300	3,400	50	540
Formaldehyde				
Main process incinerator	0	15,000	0	2,300
Naphthoquinone				
Main process incinerator	–[a]	–[a]	0	1,300
Secondary incinerator	–[a]	–[a]	500	7,000
Vanadium oxide catalyst				
Catalyst storage	–[a]	–[a]	40	650

[a] No emissions.

SECTION III

SOURCE DESCRIPTION

A. PROCESS DESCRIPTION

The first commercial phthalic anhydride process was patented by Badische Anilin und Soda-Fabrik (BASF) in Germany in 1896. The process utilized the liquid-phase oxidation of naphthalene in concentrated sulfuric acid in the presence of mercury sulfate.[1] In 1917, a catalytic vapor-phase process for the oxidation of naphthalene was developed in both the United States and Germany. Phthalic anhydride was first produced by the vapor-phase oxidation of xylene in 1946 in the United States.[2] o-Xylene has now become the preferred raw material due to its lower cost and somewhat better yield ratio compared with naphthalene. At present, all units in the world, with the exception of Progil in France, use vapor-phase processes. In 1975, 67% of the phthalic anhydride produced in the continental United States was obtained from o-xylene and 33% from naphthalene as shown in Figure 1 (and in Table 20).[3,4]

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[1] Ockerbloom, N. E. Xylenes and Higher Aromatics, Part 3: Phthalic Anhydride. Hydrocarbon Processing. 22:162-166, September 1971.

[2] Landau, R., and H. Harper. Phthalic Anhydride. Chemistry and Industry (London). July 29, 1961, p. 1143-1152.

[3] Phthalic Anhydride. Chemical Marketing Reporter. 205:9, March 4, 1974.

[4] Anderson, E. V. Phthalic Anhydride Makers Foresee Shortage. Chemical and Engineering News. 53:10-11, June 30, 1975.

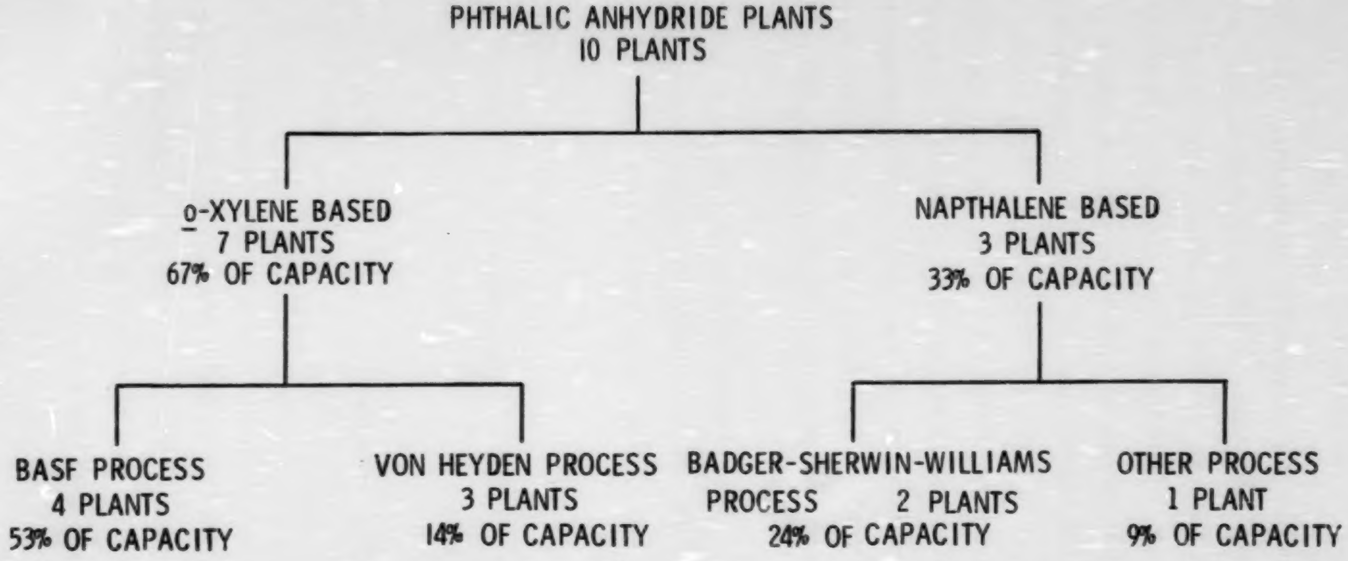
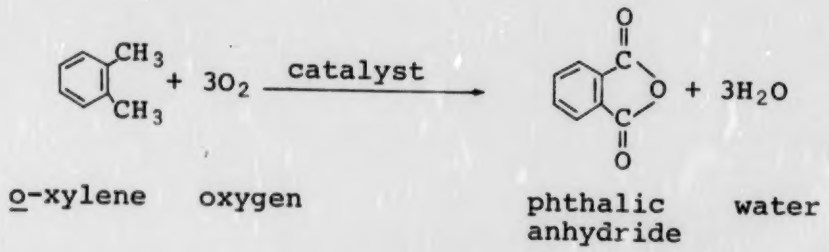

PHTHALIC ANHYDRIDE PLANTS
10 PLANTS
o-XYLENE BASED
7 PLANTS
67% OF CAPACITY
NAPTHALENE BASED
3 PLANTS
33% OF CAPACITY
BASF PROCESS
4 PLANTS
53% OF CAPACITY
VON HEYDEN PROCESS
3 PLANTS
14% OF CAPACITY
BADGER-SHERWIN-WILLIAMS
PROCESS 2 PLANTS
24% OF CAPACITY
OTHER PROCESS
1 PLANT
9% OF CAPACITY

Figure 1. Breakdown of phthalic anhydride production in the continental United States

1. o-Xylene Based Process

Phthalic anhydride is presently produced in the United States from o-xylene by the von Heyden process, which is licensed in somewhat different forms by Chemiebau and Lurgi, and by the BASF process, developed in the late 1960's. In 1975, 79% of the o-xylene based production in the continental United States involved use of the BASF process and 21% utilized the von Heyden process.[3,4] Figure 2 is a schematic flow diagram for the BASF process, which is described in the following subsections. The numbered streams in Figure 2 are identified in Table 6. Since the gross features of the von Heyden process differ only in minor ways from the BASF process, the former will not be described *per se*.

a. Chemistry - The vapor-phase oxidation of o-xylene to phthalic anhydride on a vanadium oxide catalyst can be represented by the following equation:



The principal side reactions are the result of the further oxidation of phthalic anhydride to maleic anhydride, carbon oxides, and water. Based on the work of Bernardini and Ramacci,[5] the main sequence of reactions in the oxidation of o-xylene is as follows:

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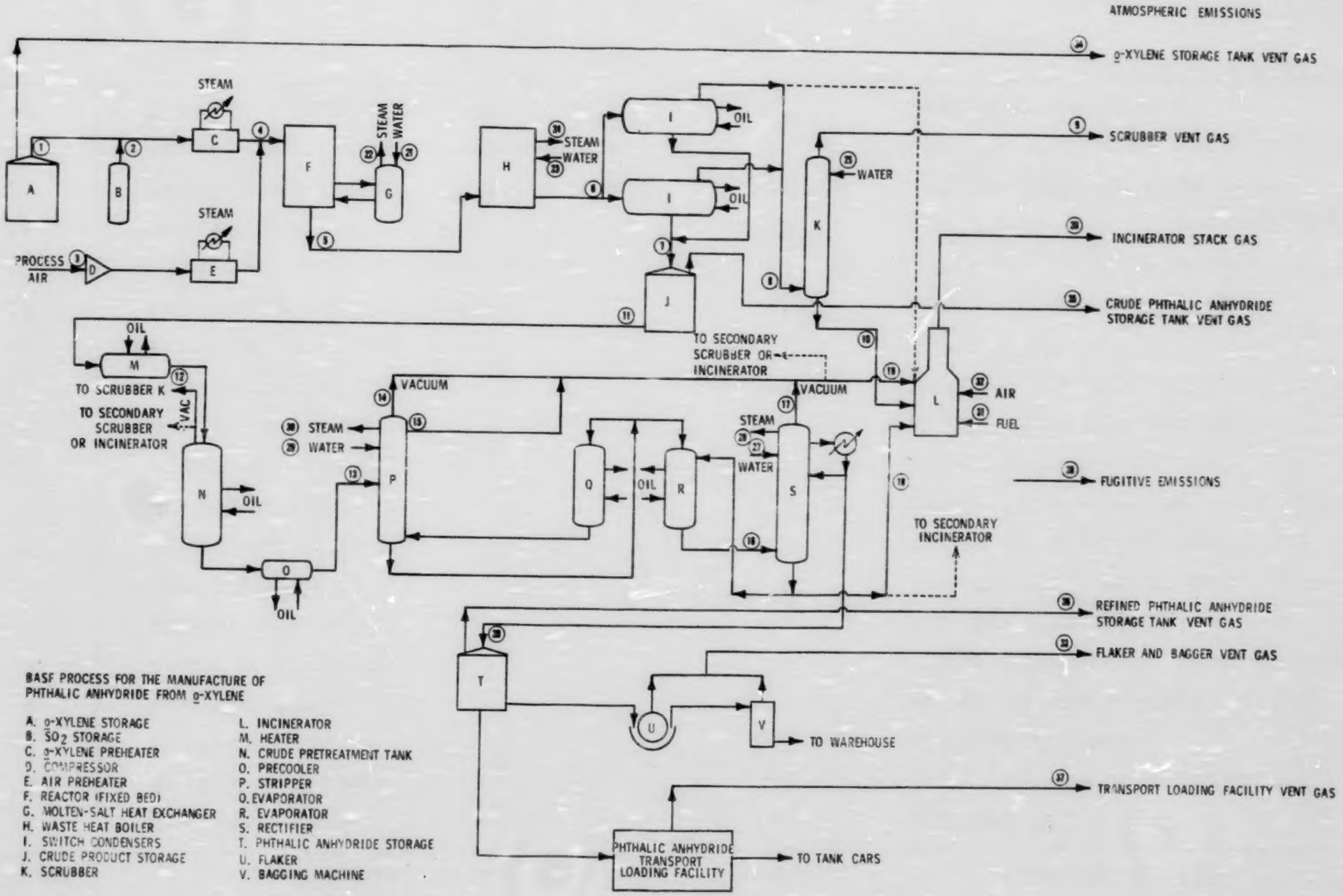
[5] Bernardini, F., and M. Ramacci. Oxidation Mechanism of o-Xylene to Phthalic Anhydride. Chimica e l'Industria (Milan). 48:9-17, January 1966.


ATMOSPHERIC EMISSIONS
o-XYLENE STORAGE TANK VENT GAS
SCRUBBER VENT GAS
INCINERATOR STACK GAS
CRUDE PHTHALIC ANHYDRIDE STORAGE TANK VENT GAS
FUGITIVE EMISSIONS
REFINED PHTHALIC ANHYDRIDE STORAGE TANK VENT GAS
FLAKER AND BAGGER VENT GAS
TRANSPORT LOADING FACILITY VENT GAS
STEAM
STEAM
STEAM
WATER
PROCESS AIR
OIL
VACUUM
VAC
AIR
FUEL
TO SECONDARY SCRUBBER OR INCINERATOR
TO SCRUBBER K
TO SECONDARY INCINERATOR
TO WAREHOUSE
TO TANK CARS
PHTHALIC ANHYDRIDE TRANSPORT LOADING FACILITY
A
B
C
D
E
F
G
H
I
J
K
L
M
N
O
P
Q
R
S
T
U
V
1
2
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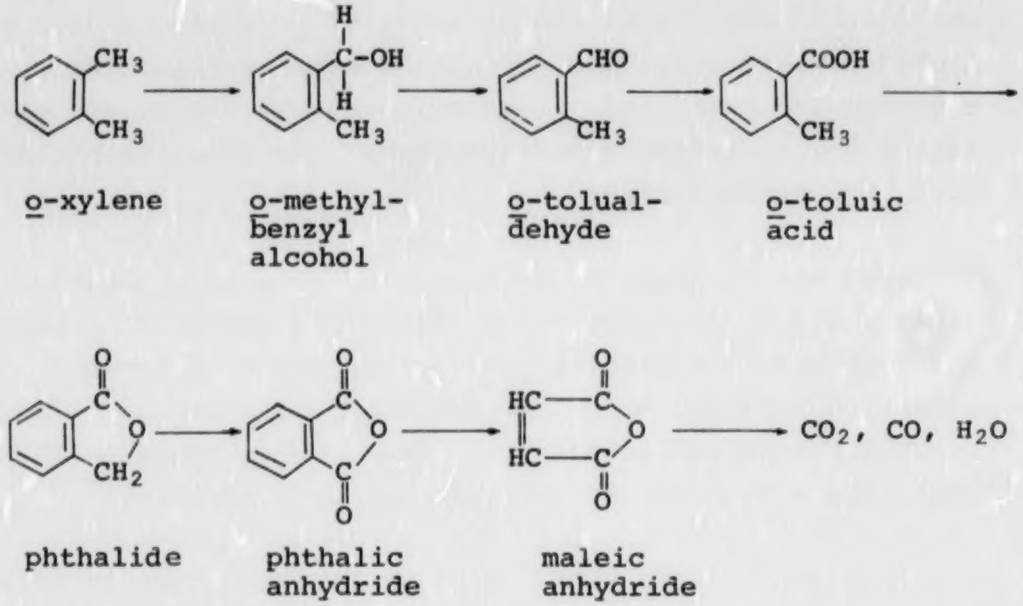
30
BASF PROCESS FOR THE MANUFACTURE OF PHTHALIC ANHYDRIDE FROM o-XYLENE
A. o-XYLENE STORAGE
B. SO2 STORAGE
C. o-XYLENE PREHEATER
D. COMPRESSOR
E. AIR PREHEATER
F. REACTOR (FIXED BED)
G. MOLTEN-SALT HEAT EXCHANGER
H. WASTE HEAT BOILER
I. SWITCH CONDENSERS
J. CRUDE PRODUCT STORAGE
K. SCRUBBER
L. INCINERATOR
M. HEATER
N. CRUDE PRETREATMENT TANK
O. PRECOOLER
P. STRIPPER
Q. EVAPORATOR
R. EVAPORATOR
S. RECTIFIER
T. PHTHALIC ANHYDRIDE STORAGE
U. FLAKER
V. BAGGING MACHINE

Figure 2. BASF process for manufacture of phthalic anhydride from o-xylene

Table 6. STREAM CODE FOR BASF PROCESS ILLUSTRATED IN FIGURE 2

Stream	Identification	Stream	Identification
1	o-Xylene feed	20	Refined PAN
2	Sulfur dioxide	21	Water to steam generator
3	Filtered air	22	Generated steam
4	Reactor feed	23	Water to waste-heat boiler
5	Reactor product	24	Steam from waste-heat boiler
6	Boiler effluent	25	Scrubber makeup
7	Crude product	26	Incinerator stack gas
8	Condenser off-gas	27	Water to cooling coil
9	Scrubber vent	28	Steam from cooling coil
10	Scrubber liquid purge	29	Water to cooling coil
11	Crude PAN product	30	Steam from cooling coil
12	Pretreatment exhaust	31	Incinerator fuel
13	Pretreated crude	32	Combustion air
14	Stripping column exhaust	33	Flaker and bagger vent
15	Stripping column overhead	34	o-Xylene storage vent
16	Rectifying column feed	35	Crude product storage vent
17	Rectifying column vacuum exhaust	36	Refined PAN storage vent
18	Rectifying column bottom product	37	Loading facility vent
19	Distillation light ends	38	Fugitive emissions


o-xylene
o-methylbenzyl alcohol
o-tolualdehyde
o-toluic acid
phthalide
phthalic anhydride
maleic anhydride
CO2, CO, H2O

Direct oxidation of o-xylene or any of the intermediates to carbon oxides and water can also occur. A certain amount of bypassing of intermediates in the sequence is also possible. In addition, many other reactions are possible. For example, Bernardini and Ramacci presented a scheme containing 21 compounds and 31 reaction arrows.[5]

b. Feed Materials - Feed materials used in the BASF process consist of o-xylene, air, and sulfur dioxide. The xylene feed (stream 1 in Figure 2) contains 95% by weight o-xylene, the remainder consisting of *meta-* and *para-*xylenes (designated as m- and p-xylenes). Only the o-xylene can form phthalic anhydride. The m- and p-xylenes are reportedly converted to carbon oxides and water under commercial reactor conditions.[6] However, Bhattacharyya and Gulati[7] state that the products of p-xylene oxidation include maleic anhydride, p-tolualdehyde, p-toluic acid, terephthalic acid, and p-benzoquinone, while m-xylene oxidation yields maleic anhydride, m-tolualdehyde, isophthalic acid, and p-benzoquinone.

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[6] Friedrichsen, W., et al. Production of Phthalic Anhydride. British Patent No. 1,082,326 (to BASF), September 6, 1967.

Filtered air (stream 3) is compressed to a gage pressure of 48.2 kPa to 55.2 kPa and preheated to 149°C using steam. The liquid xylene feed is also preheated and vaporized by injection into the hot air stream. A small amount (0.5-2.5% by weight[6]) of sulfur dioxide (stream 2) is added to the feed stream in order to maintain catalyst activity.[a]

c. Reactor - In the BASF process, the weight ratio of air to xylene in the feed stream (stream 4) to the reactor (unit F) is 25, which is equivalent to 1 mole percent xylene (weight ratios as low as 20 and as high as 34 have been reported in the literature).[8] Excess air is employed to ensure that the mixture is below the lower explosive limit of 1.5 mole percent o-xylene.[9] After removal of unvaporized feed, the reactants are fed to the fixed-bed reactor, which operates at about 380°C within a range of 300-390°C.[6,9]

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[a] The active form of the catalyst contains a mixture of V^{+5} and V^{+4}. The role of the SO_2 is to adjust the redox conditions so as to maintain the V^{+4}/V^{+5} ratio within an optimum range of from one to nine.[6]

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[7] Bhattacharyya, S. K., and I. B. Gulati. Catalytic Vapor-Phase Oxidation of Xylenes. Industrial and Engineering Chemistry. 50:1719-1726, December 1958.

[8] Spitz, P. H. Phthalic Anhydride Revisited. Hydrocarbon Processing. 47:162-168, November 1968.

[9] Schwab, R. F., and W. H. Doyle. Hazards in Phthalic Anhydride Plants. Chemical Engineering Progress. 66:49-53, September 1970.

The BASF reactor has a capacity of approximately 1.44 x 10^4 metric tons/yr and a diameter of 4.2 m.[8] The reactor contains 9,948 catalyst-filled tubes which are 25.4 mm in diameter and 3 m long.[8] (A larger version of this reactor containing approximately 13,000 tubes is also used in some plants.) A typical BASF plant consists of four reactors which can be split to operate on two production trains.[10] A molten salt (sodium-potassium nitrate-nitrite eutectic)[9] is circulated on the shell side of the reactor to remove the heat produced in the exothermic reaction. The molten salt passes through an external heat exchanger (unit G) where high pressure steam is produced. The gases leave the reactor at 375°C (stream 5) and pass through a waste heat boiler (unit H) for additional steam generation.

The conversion of the xylene in the reactor is 100%, with a maximum yield of 1.03 kg phthalic anhydride per kilogram of 95% o-xylene feed.[11] (The theoretical yield is 1.39 kg per kilogram of 100% o-xylene.[1])

d. Switch Condensers - Due to the excess (567%) of air employed in the reactor, the partial pressure of the phthalic anhydride in the effluent gas stream is such that the dew point is below the melting point (130.8°C) of phthalic anhydride. Hence, the product condenses as a solid. This operation is carried out in a parallel bank of tubular condensers (unit I) which are alternately heated and cooled by separate heat-transfer oil streams on an automatically controlled cycle. During the cooling portion of the cycle, phthalic anhydride crystallizes on the outer surfaces of the finned tubes. During the heating portion of the cycle, the solid phthalic anhydride is melted and then transferred to the crude product storage tank (unit J). A typical operation[12] employs a sequence of nine individual condensers, with six condensing and two melting at any given time. The ninth unit is on standby to allow for periodic cleaning and maintenance without disruption of service. Residual gases from the condensers (stream 8) at a temperature of 66°C and gage pressure of 26 kPa are sent to a water scrubber (unit K) or, in some plants, directly to an incinerator (unit L).

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[10] Phthalic Anhydride: Return to Overcapacity. Chemical and Engineering News. 49:18-19, March 15, 1971.

[11] Phthalic Anhydride by Vapor-Phase Oxidation. The Oil and Gas Journal. 71:92, March 12, 1973.

e. Product Purification - The crude product, which contains 99% to 99.5% phthalic anhydride as phthalic acid,[11] is stored at 149°C under atmospheric pressure. The refining operation consists of two steps: a heat treatment step followed by a vacuum distillation. The crude product (stream 11) passes through a preheater (unit M) and then to the pretreatment tank (unit N), where it is held at an elevated temperature under vacuum for 8 to 12 hours. The purpose of the heat treatment is to decompose color-forming compounds and to convert them to higher molecular weight materials that can be separated from the main product by distillation. At the same time, dissolved phthalic acid is dehydrated to the anhydride, and the associated water and other low-boiling materials, such as maleic anhydride and benzoic acid, are partially evaporated and removed through the vacuum jet ejector exhaust stream (stream 12). This exhaust stream is sent to either the scrubber (unit K) or a separate control device (which may be another scrubber or another incinerator).

The pretreatment tank is discharged to a continuous distillation system consisting of a stripping column (unit P) and a rectifying column (unit S), both of which operate in the range of 2.67 kPa to 26.7 kPa absolute pressure. The discharge stream passes through a precooler (unit O) and enters the stripping column at about 186°C. Maleic anhydride and benzoic acid are separated in the overhead stream (stream 15) which is sent to the main incinerator (unit L) or to a secondary control device (via stream 19) for disposal. The bottom stream from the stripping column passes to the evaporators (reboilers, units Q and R). Part of the stream is recycled to the stripping column, and the remainder (stream 16) enters the rectifying column (unit S).

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[12] Riley, H. L. How to Design and Operate Fluidized-Catalyst PA Plants. Hydrocarbon Processing and Petroleum Refiner. 42:167-172, June 1963.

The bottom stream (stream 18) from the rectifying column (the residue) is sent to the main incinerator or a secondary incinerator for disposal. Phthalic anhydride (99.99%) is taken overhead, condensed, and sent to the product storage tank (unit T) where it is stored at atmospheric pressure and 149°C.

The phthalic anhydride in the storage tanks can be pumped to tank cars for shipment as a liquid, or it can be sent to a flaking machine (unit U) for solidification. The flaked product is weighed and packaged in 36-kg bags by a bagging machine (unit V).

f. *Incinerators* - The switch-condenser off-gas may be treated either by a scrubber-incinerator combination or by direct incineration. These operations are common to both the *o*-xylene and naphthalene based plants. The scrubber-incinerator combination is discussed in Section III.A.2.g, "Naphthalene Based Process," since the available data are for a naphthalene based plant. A dual incineration system, which is currently in operation on a 5.9×10^4 metric tons/yr *o*-xylene based plant, is described below. Either system should be equally applicable to *o*-xylene and naphthalene based operations.

The dual incineration system employs two thermal incinerators, one of which treats the switch-condenser off-gas while the other treats all of the waste streams from the product purification section of the plant. However, in the plant currently using the system, the switch-condenser off-gas is handled by two parallel incinerators, one on each of the two production trains. The total phthalic anhydride design capacity of this system is 8.84×10^4 metric tons/yr.

The two parallel incinerators incorporate waste-heat boilers which produce steam at 400°C and a gage pressure of 4,480 kPa.[13] The incinerators operate at 700°C to 760°C and the combusted gases exit from the stacks at 250°C. The reported control efficiency of this unit is 99.9% for carbon monoxide and 96.5% for combined organics when operating at 760°C.[13]

The secondary incinerator used to treat the waste streams from the product purification section of the plant is designed to handle overheads and residues, and burns natural gas to maintain an operating temperature of 650°C. The reported control efficiency achieved by the unit is 99% for combined organics.[13]

g. Storage Tanks - The feedstock, crude product, and refined product storage tank requirements for a typical 5.9×10^4 metric tons/yr o-xylene based phthalic anhydride plant are summarized in Table 7.[13]

Conservation vents can be used on o-xylene storage tanks to minimize breathing losses. The breather valves are set to open between 1.0 kPa and 1.47 kPa pressure.[14] o-Xylene is

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[13] Personal communication, H. M. Lacy, Monsanto Company. April 7, 1975.

[14] Fawcett, R. L. Air Pollution Potential of Phthalic Anhydride Manufacture. Journal of the Air Pollution Control Association. 20:461-465, July 1970.

Table 7. SUMMARY OF TANKAGE REQUIREMENTS FOR A 5.9 x 10^4 METRIC TONS/YR o-XYLENE BASED PHTHALIC ANHYDRIDE PLANT

Tank no.[a]	Material stored	Capacity, m^3	Turnovers per year
1	o-Xylene	329	230
2	o-Xylene	3,331	23
3	Crude product	360	65
4	Crude product	360	65
5	Phthalic anhydride	341	72
6	Phthalic anhydride	341	72
7	Phthalic anhydride	379	44
8	Phthalic anhydride	757	44

[a] Detailed storage tank calculations are shown in Appendix A.

stored at ambient temperature and has a vapor pressure of from 0.13 kPa to 1.47 kPa under these conditions. The tanks may also be blanketed with nitrogen to prevent the formation of an explosive mixture in the vapor space above the liquid xylene.

Crude and refined phthalic anhydride storage tanks are maintained at 149°C to 160°C, at which temperatures the vapor pressure is 2.27 kPa to 3.33 kPa. The tanks are blanketed with dry nitrogen to prevent the entry of oxygen and water vapor. The former creates a fire hazard while the latter results in the hydrolysis of phthalic anhydride to phthalic acid. Conservation vents are not used on these tanks because the phthalic anhydride vapors tend to solidify and plug the vents. Control can be maintained by venting the tanks to the incinerator or by the use of condensers or sublimation boxes in which the phthalic anhydride is removed from the vent stream by condensation and solidification.

h. Heat-Transfer Circuits - The BASF process employs three heat-transfer fluid systems: (1) a molten salt system which removes heat from the reactor (units F and G in Figure 2); (2) an organic fluid (e.g., Dowtherm A, a diphenyl-diphenyl oxide eutectic) system that heats and cools the switch condensers (units I); and (3) an organic fluid system which services the product purification section (units M, N, O, Q, R). Molten salt heat exchange systems and organic systems are described in the literature.[15,16-22]

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[15] Uhl, V. W., and H. P. Voznick. Molten Salt as a Heat Transfer Medium. Chemical Engineering Progress. 59:33-35, May 1963.

[16] Fried, J. R. Heat-Transfer Agents for High-Temperature Systems. Chemical Engineering. 80:89-98, May 28, 1973.

[17] Seifert, W. F., L. L. Jackson, and C. E. Sech. Organic Fluids for High-Temperature Heat-Transfer Systems. Chemical Engineering. 79:96-104, October 30, 1972.

[18] Purdy, R. B., et al. Indirect Heating with Aromatic Oils. Chemical Engineering Progress. 59:43-46, May 1963.

[19] Conant, A. R., and W. F. Seifert. Dowtherm Heat Transfer Medium. Chemical Engineering Progress. 59:46-49, May 1963.

[20] Petersen, D. E., and R. K. Bedell. UCON Heat Transfer Fluid. Chemical Engineering Progress. 59:36-39, May 1963.

[21] Davis, W. J., and P. G. Benignus. Therminol FR-2 Heat Transfer Systems. Chemical Engineering Progrsss. 59:39-42, May 1963.

[22] Frikken, D. R., K. S. Rosenberg, and D. E. Steinmeyer. Understanding Vapor-Phase Heat-Transfer Media. Chemical Engineering. 82:86-90, June 9, 1975.

Details of the heat-transfer circuits employed in phthalic anhydride plants are not available. However, the essential features of the organic fluid systems are illustrated in the basic liquid-phase heat-transfer system shown in Figure 3. Heat-transfer fluid is pumped from the direct-fired heater to the user system. A surge tank is located on the suction side of the pump in order to accommodate thermal expansion of the liquid during startup and surging due to the venting of line-trapped steam.

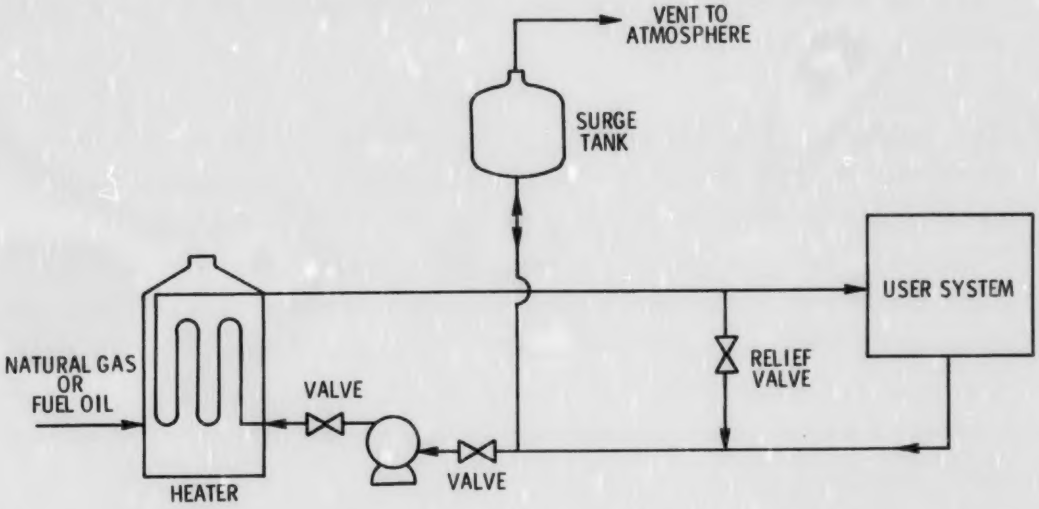

Figure 3. Organic liquid heat-transfer system

Surge tanks are normally designed for maximum temperatures of 50°C to 60°C in order to provide a cold-fluid seal to the atmosphere, thereby minimizing fluid oxidation. In order to achieve these temperatures, tanks are not insulated, and may be water jacketed. The surge tank is vented to the atmosphere when the vapor pressure of the fluid is sufficiently low to permit an unpressurized system and the fluid is sufficiently stable to air oxidation. Higher vapor pressure fluids require system pressurization, which can be accomplished by blanketing the surge tank with an inert gas.

i. Waste Water Streams - One source of waste water in phthalic anhydride plants is the steam boiler blowdown, which amounts to 0.52 kg per kilogram of phthalic anhydride.[13] Another source of waste water in some plants is the secondary scrubber used to control the waste streams from the product purification section of the plant. The liquid purge from this scrubber must either be incinerated or sent to a waste water treatment facility.

j. Plant Shutdown, Turnaround, and Start-up - Data on o-xylene based phthalic anhydride plant shutdowns, turnarounds, and start-ups were obtained from industry.[13] Phthalic anhydride plants are shut down on an average of once per year. During start-up, the reactor is brought to operating temperature by heating the process air in a natural gas heater. The mixture of hot air and combustion gases is passed through the reactor and then vented directly to the atmosphere.

Start-up or other operating upsets can result in emissions of heat-transfer fluid (designated "oil" in Figure 2) from surge tank vents in the heat-transfer circuits associated with the switch condensers and with the product purification section of the plant. The emissions are in the form of an aerosol mist, which reportedly settles in the immediate vicinity of the emission point due to the low vapor pressure of the heat-transfer fluid. These emissions are estimated to be 0.016 g/kg phthalic anhydride, of which 95% is estimated to originate from the switch-condenser circuit.[13]

k. Catalyst - Many variations of the vanadium oxide catalyst are possible.[6] In one example,[6] the catalyst consists of 3.75 wt % vanadium oxide (as V_2O_5) and 21.25 wt % potassium pyrosulfate on a titanium dioxide carrier (75 wt %). To activate the catalyst, about 65% of the vanadium is converted to the tetravalent state by heating in air containing SO_2. Under the reaction conditions, the vanadium oxide-potassium pyrosulfate mixture is present as a melt in the pores of the TiO_2 carrier which has a grain size of 0.2 mm to 0.5 mm.

In a study of vanadium oxide catalyzed oxidation reactions, Simard, et al.[23] concluded that the organic oxidations take place at the surface of the catalyst through ionic reactions. Based on this observation, one possible mechanism for the reaction is indicated in Figure 4. Simard, et al. postulated that the surface layer of the catalyst is composed of oxygen ions and pentavalent vanadium ions in the geometrical arrangement shown. In Step 1, an o-xylene molecule is adsorbed on the catalyst surface. In Step 2, a hydrogen ion is removed from the hydrocarbon by a surface oxygen ion, and an electron from the hydrocarbon is transferred to a vanadium ion. In Step 3, a covalent bond is formed between the available carbon atom and the hydroxide group and an electron is transferred from the organic molecule to a vanadium ion. In the fourth step, the organic molecule (o-methylbenzyl alcohol) is desorbed from the surface leaving a vacant site on the surface. Following this, an oxygen atom from an oxygen molecule in the gas phase would fill the vacant site and be reduced to a minus

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[23] Simard, G. L., et al. Vanadium Oxides as Oxidation Catalysts. Industrial and Engineering Chemistry. 47:1424-1430, July 1955.

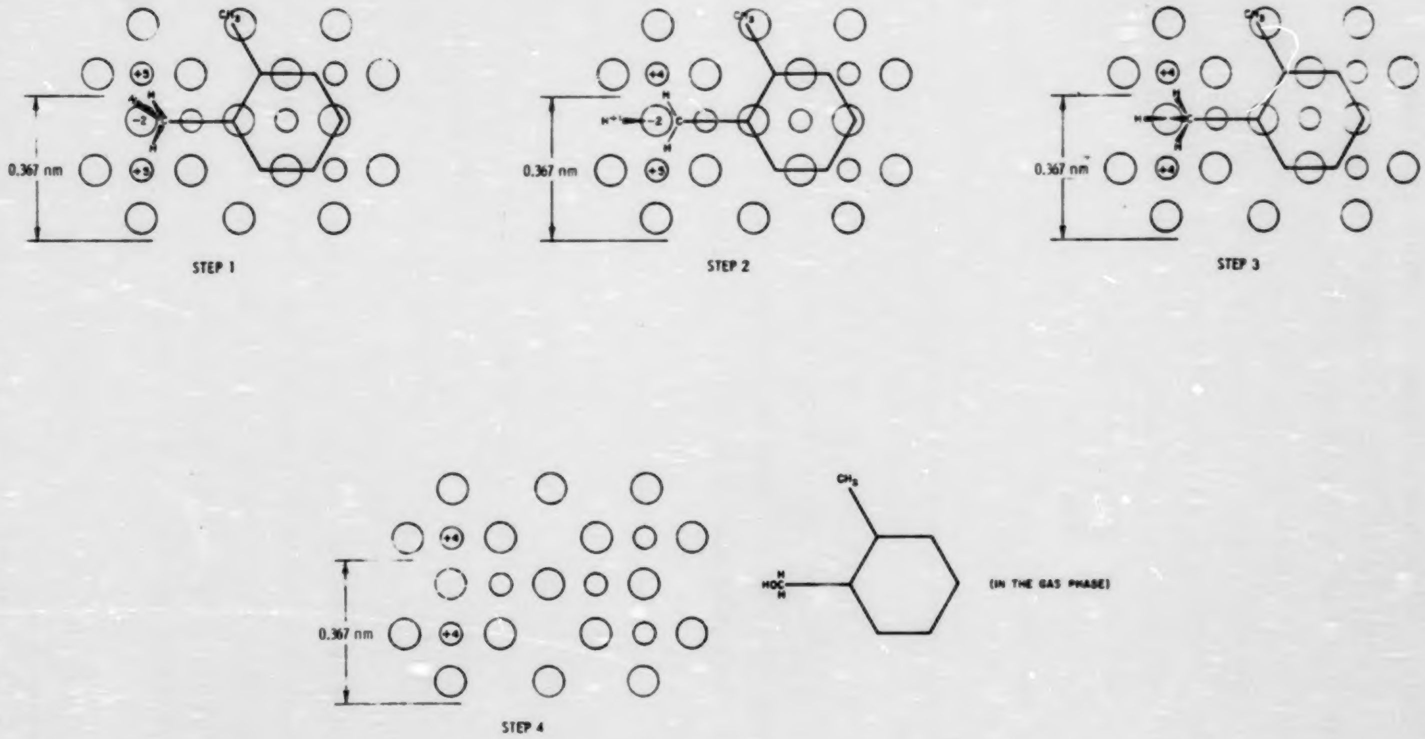
CH3
+5
-2
H
C
0.367 nm
STEP 1
+4
H+
-2
+5
0.367 nm
STEP 2
+4
0.367 nm
STEP 3
+4
0.367 nm
STEP 4
CH3
HOC
(IN THE GAS PHASE)

Figure 4. Reaction mechanism for the catalytic oxidation of o-xylene

2 valence while the two adjacent V^{+4} ions would be oxidized to V^{+5}. Further oxygen atoms would then be added to the organic molecule in a similar fashion.

Alternatively, the reaction could proceed via oxygen ions adsorbed on the catalyst surface rather than incorporated in the lattice. In either case, electrons must be transferred from donor sites in the catalyst to oxygen atoms in order to form oxygen ions. The catalytic activity of the vanadium oxide is due in part to the fact that it is a semiconductor (n-type) which facilitates these electron transfer processes.[24]

The following three-stage mechanism for the oxidation of sulfur dioxide on a vanadium oxide catalyst has been proposed by Glueck and Kenney:[25]

$$V_2O_5 \cdot SO_3 + SO_2 \longrightarrow (VOSO_4)_2$$

$$(VOSO_4)_2 \longrightarrow V_2O_4 \cdot SO_3 + SO_3$$

$$V_2O_4 \cdot SO_3 + 1/2\ O_2 \longrightarrow V_2O_5 \cdot SO_3$$

In the above equations, $V_2O_5 \cdot SO_3$ represents vanadium pentoxide in the melt associated with sulfur trioxide formed from the decomposition of the pyrosulfate anion. The result of the first two steps is the reduction of vanadium from the pentavalent to the tetravalent state. This provides an explanation of the role of the sulfur dioxide in maintaining the V^{+4}/V^{+5} balance in the catalyst.

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[24] Cullis, C. F. Heterogeneous Catalytic Oxidation of Hydrocarbons. Industrial and Engineering Chemistry. 59:18-27, December 1967.

[25] Glueck, A. R., and C. N. Kenney. The Kinetics of the Oxidation of Sulphur Dioxide Over Molten Salts. Chemical Engineering Science. 23:1257-1265, 1968.

1. Reactor System Heat Balance - The oxidation of o-xylene is an exothermic chemical reaction. The standard heats of reaction for the main reaction and principal side reactions were calculated on the basis that all of the compounds involved are in the vapor state, and the results are listed in Table 8. The heat released in a commercial reactor has been estimated to be 17.1 MJ/kg[a] phthalic anhydride formed,[26] and this value agrees well with an estimate based on the data in Table 8.

Table 8. HEATS OF REACTION FOR THE OXIDATION OF o-XYLENE

Reaction	Heat of reaction	
	MJ/kg	MJ/kg mol
o-Xylene + $3O_2$ → phthalic anhydride + $3H_2O$	12.5	1,286
o-Xylene + $7.5O_2$ → maleic anhydride + $4CO_2$ + $4H_2O$	28.2	2,983
o-Xylene + $10.5O_2$ → $8CO_2$ + $5H_2O$	41.2	4,387

The heat of reaction is used to generate steam in the molten-salt heat exchanger and in the waste-heat boiler. Part of this steam is used to satisfy process requirements and the remainder is available for export. A representative energy balance for a phthalic anhydride plant is given in Table 9.

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[a] 1 MJ = 1 x 10^6 joules = 948 Btu (see Section IX).

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[26] Schwartz, W. A., et al. Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry, Volume 7: Phthalic Anhydride Manufacture from Ortho-xylene. Air Products and Chemicals, Inc., Houdry Division. U.S. Environmental Protection Agency. Research Triangle Park. Publication EPA-450/3-73-006-g, July 1975. 108 p.

Table 9. REACTOR SYSTEM HEAT BALANCE FOR PRODUCTION OF PHTHALIC ANHYDRIDE FROM *o*-XYLENE[a]

Heat in	MJ/kg PAN
Exothermic heat of reaction	17.1
Feed preheat	3.8
TOTAL	20.9

Heat out	MJ/kg PAN
Steam generation	
Reactor internal cooling	10.6
Waste heat boiler	6.0
Reactor heat losses	0.1
Switch condensers	3.3
Incremental effluent heat content[b]	0.9
TOTAL	20.9

[a] Basis:
Table 18 Material Balance.
Xylene feed at 26.7°C, air at 26.7°C.
Feed preheated to 149°C.
Reactor outlet temperature, 375°C.
Condenser effluent gas at 65.6°C.
Effluent from waste heat boiler at 163°C.

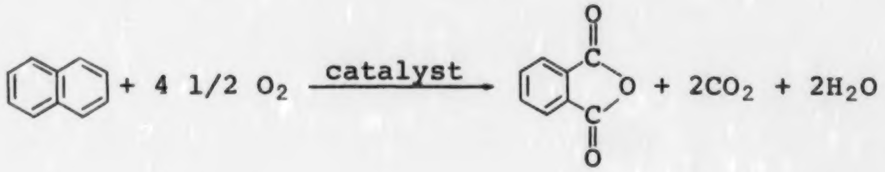
[b] Difference in heat content between condenser effluent streams and reactor feed streams.

2. Naphthalene Based Process

All of the phthalic anhydride currently produced from naphthalene in the United States is made via the fluid-bed process. Two of the three plants now in operation, which account for 73% of the naphthalene based production, use the Badger-Sherwin-Williams process, first commercialized in the early 1960's. The Koppers Company plant in Bridgeville, Pennsylvania, uses a fluid-bed process developed by

American Cyanamid, which built and operated the plant in the 1950's. This process was never licensed, and the plant was eventually taken over by Koppers when they acquired all of Cyanamid's facilities at the Bridgeville location.[8] Figure 5 is a schematic flow diagram for the Badger-Sherwin-Williams process, which is described below. Process streams numbered in Figure 5 are identified in Table 10.

a. Chemistry - The vapor-phase oxidation of naphthalene to phthalic anhydride on a vanadium oxide catalyst can be represented by the following equation:



naphthalene oxygen phthalic anhydride carbon dioxide water

The side reactions are the consequence of the further oxidation of phthalic anhydride to maleic anhydride, carbon oxides, and water. Based on the work of Ioffe, et al.,[27] the main sequence of reactions in the oxidation of naphthalene is as follows:

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[27] Ioffe, I. I., et al. Kinetics and Vapor Phase Oxidation Mechanism of Aromatic Hydrocarbons. VI. Zhurnal Fizicheskoi Khimii (Journal of Physical Chemistry). 29:692-698, 1955.

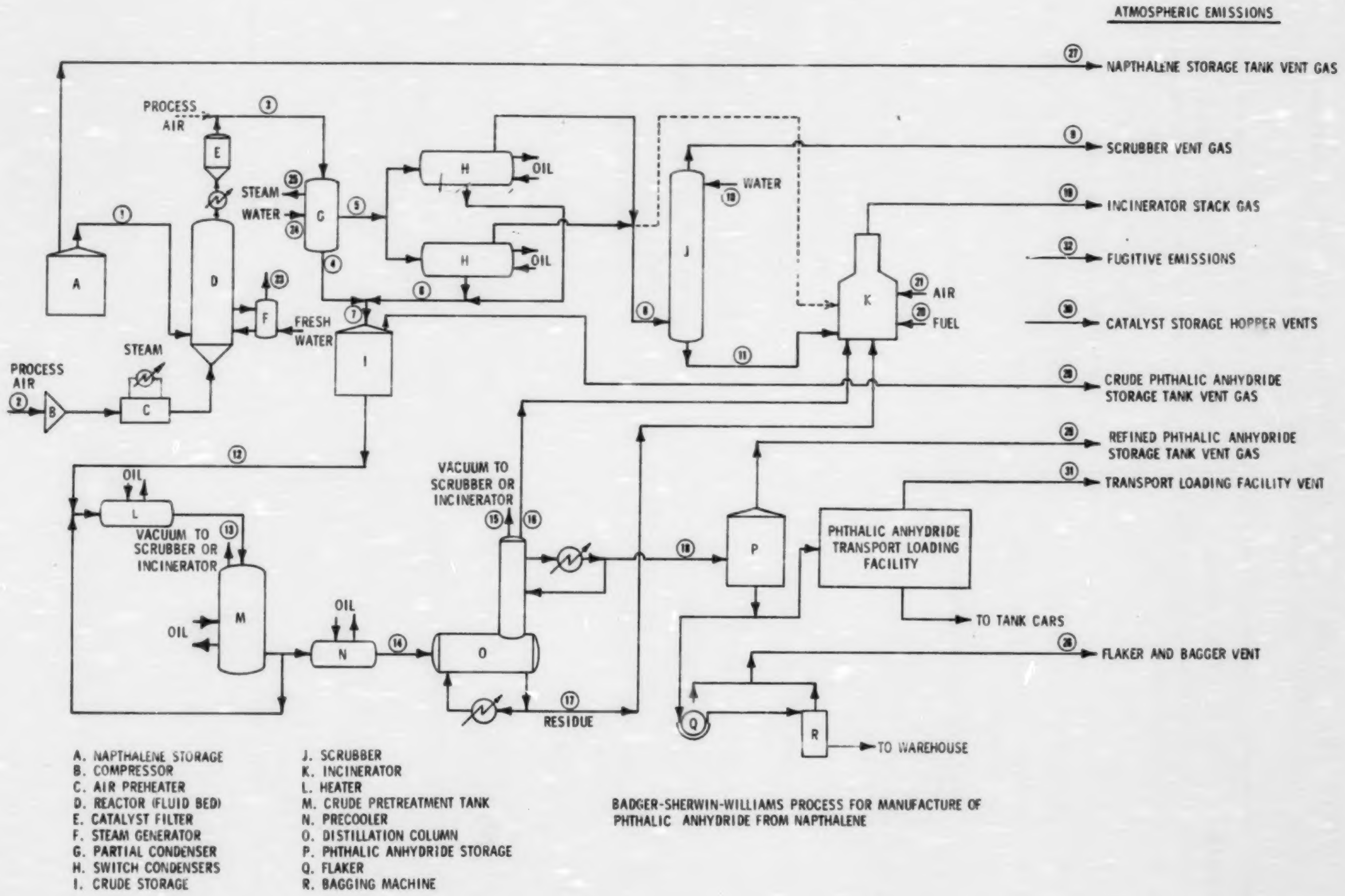
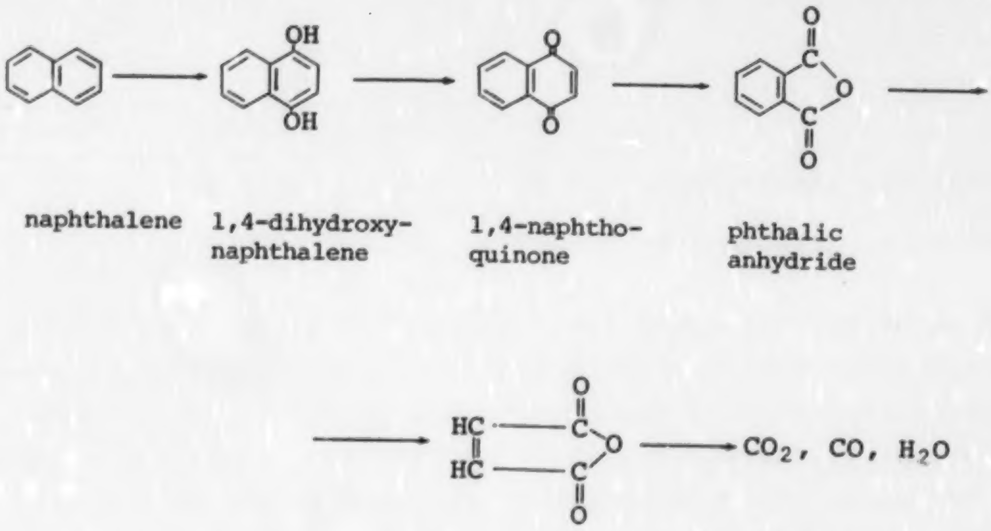

ATMOSPHERIC EMISSIONS
27 NAPTHALENE STORAGE TANK VENT GAS
9 SCRUBBER VENT GAS
19 INCINERATOR STACK GAS
22 FUGITIVE EMISSIONS
30 CATALYST STORAGE HOPPER VENTS
28 CRUDE PHTHALIC ANHYDRIDE STORAGE TANK VENT GAS
29 REFINED PHTHALIC ANHYDRIDE STORAGE TANK VENT GAS
31 TRANSPORT LOADING FACILITY VENT
26 FLAKER AND BAGGER VENT
PROCESS AIR
2
PROCESS AIR
3
1
STEAM
25
WATER
24
23
FRESH WATER
4
5
6
7
8
OIL
OIL
WATER
10
11
AIR
21
FUEL
20
12
OIL
VACUUM TO SCRUBBER OR INCINERATOR
13
OIL
OIL
14
VACUUM TO SCRUBBER OR INCINERATOR
15
16
17
RESIDUE
18
PHTHALIC ANHYDRIDE TRANSPORT LOADING FACILITY
TO TANK CARS
TO WAREHOUSE
A
B
C
D
E
F
G
H
H
I
J
K
L
M
N
O
P
Q
R
A. NAPTHALENE STORAGE
B. COMPRESSOR
C. AIR PREHEATER
D. REACTOR (FLUID BED)
E. CATALYST FILTER
F. STEAM GENERATOR
G. PARTIAL CONDENSER
H. SWITCH CONDENSERS
I. CRUDE STORAGE
J. SCRUBBER
K. INCINERATOR
L. HEATER
M. CRUDE PRETREATMENT TANK
N. PRECOOLER
O. DISTILLATION COLUMN
P. PHTHALIC ANHYDRIDE STORAGE
Q. FLAKER
R. BAGGING MACHINE
BADGER-SHERWIN-WILLIAMS PROCESS FOR MANUFACTURE OF PHTHALIC ANHYDRIDE FROM NAPTHALENE

Figure 5. Badger-Sherwin-Williams process for manufacture of phthalic anhydride from naphthalene

Table 10. STREAM CODE FOR BADGER-SHERWIN-WILLIAMS PROCESS ILLUSTRATED IN FIGURE 5

Stream	Identification	Stream	Identification
1	Naphthalene	17	Distillation column bottom product
2	Air	18	Refined PAN
3	Reactor product	19	Incinerator stack gas
4	Crude from partial condenser	20	Incinerator fuel
5	Partial condenser off-gas	21	Combustion air
6	Crude from switch condenser	22	Water to steam generator
7	Crude product	23	Generated steam
8	Switch-condenser off-gas	24	Cooling water
9	Scrubber vent	25	Steam
10	Scrubber makeup	26	Flaker and bagger vent
11	Scrubber liquid purge	27	Naphthalene storage vent
12	Crude PAN	28	Crude product storage vent
13	Pretreatment vacuum exhaust	29	PAN storage vent
14	Distillation column feed	30	Catalyst storage hopper vents
15	Distillation column vacuum exhaust	31	Loading facility vent
16	Distillation column light ends	32	Fugitive emissions


OH
OH
O
O
O
C
O
C
O
naphthalene
1,4-dihydroxy-naphthalene
1,4-naphthoquinone
phthalic anhydride
HC
HC
C
O
C
O
O
CO2, CO, H2O

maleic anhydride

Direct oxidation of naphthalene or any of the intermediates to carbon oxides and water can also occur. A certain amount of bypassing of intermediates in the sequence is also possible. In addition, a reaction path involving 1,2-naphthoquinone as an intermediate has been reported in the literature.[28]

b. Feed Materials - Feed materials used in the Badger-Sherwin-Williams process consist of naphthalene and air.

Two of the naphthalene based plants use petroleum naphthalene while the other two use desulfurized coal-tar naphthalene. Typical compositions of petroleum and coal-tar naphthalene are:[29,30]

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[28] Shelstad, K. A., J. Downie, and W. F. Graydon. Kinetics of the Vapor-Phase Oxidation of Naphthalene Over a Vanadium Catalyst. Canadian Journal of Chemical Engineering. 38:102-107, August 1960.

	Wt % Naphthalene	Wt % Sulfur	Wt % Tetralin
Coal-tar naphthalene	92 - 96	0.5 - 1.0	2
Petroleum naphthalene	99.0 - 99.7	0.001	0

Present-day catalysts are capable of handling naphthalene feedstocks with sulfur content as high as 1%.[12,31] However, the sulfur in coal-tar naphthalene is principally in the form of thionaphthene, which is converted to maleic anhydride and sulfur oxides rather than phthalic anhydride.[12,32,33] The resultant loss in yield of phthalic anhydride (1% sulfur is equivalent to 4.2% thionaphthene) is apparently the primary reason for the use of desulfurized naphthalene.

The reaction products of the tetralin (1,2,3,4-tetrahydronaphthalene) present in coal-tar naphthalene are not known. The most likely products, however, are maleic anhydride, carbon oxides, and water. Some tetralin may also be

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[29] Graham, J. J., and P. F. Way. Phthalic Anhydride by Fluid Bed Process. Chemical Engineering Progress. 58:96-100, January 1962.

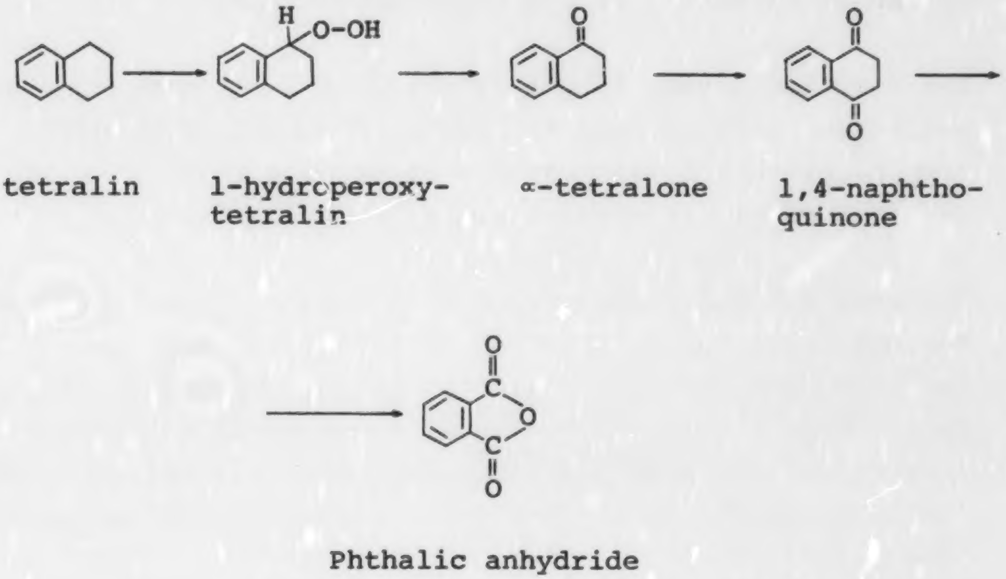
[30] Personal communication, L. B. Evans, U.S. Environmental Protection Agency (Data originally supplied by U.S. Steel Corp.). June 12, 1975.

[31] Chopey, N. P. Fluid-Bed Phthalic Anhydride. Chemical Engineering. 69:104-106, January 22, 1962.

[32] Riley, H. L. Design of Fluidized Reactors for Naphthalene Oxidation: A Review of Patent Literature. Transactions of the Institution of Chemical Engineers (London). 37:305-313, 1959.

[33] Improvements Relating to the Oxidation of Aromatic Hydrocarbons. American Cyanamid Company. British Patent No. 850,817, January 2, 1957.

converted to phthalic anhydride via a mechanism such as the following:



In this process, filtered air (stream 2 in Figure 5) is compressed and heated to 149°C. The hot air then enters the bottom of the reactor (unit D) and passes through an air distributor plate before entering the fluidized catalyst bed. Liquid naphthalene (stream 1), which is stored at 90°C to 102°C, is pumped from the storage tank (unit H) and injected directly into the fluidized bed above the air distributor plate. The naphthalene is immediately vaporized and dispersed throughout the bed upon contact with the hot catalyst and reaction air.

c. Reactor - In the Badger-Sherwin-Williams process, the weight ratio of air to naphthalene fed to the reactor is 10:1 to 12:1, which places the mixture within the explosive limits.[29] This low air to naphthalene ratio is made possible by the inerting effect of the fine catalyst particles in the fluidized bed reactor.[29,34] Within the fluid bed, a uniform temperature is maintained (to ± 5°C) in the range of 340°C to 380°C.[34] Reactor pressure is set by the backpressure of equipment downstream.

The reaction vessel itself is simply a large container of sufficient size to hold the required amount of catalyst. Single reactors having capacities of more than 4.5×10^4 metric tons/yr are feasible with the fluid-bed process.[8]

The catalyst bed is supported on a gird plate having holes through which the fluidizing air is blown. Naphthalene feed is introduced into the fluid bed through nozzles. Adequate space above the normal bed level is provided to allow for catalyst settling before the gases leave the reactor. The ratio of bed depth to diameter is about 3:1 and the contact time during reaction is 10 to 20 seconds.[29]

Removal of the heat produced by the exothermic reaction is accomplished by means of cooling tubes located directly in the catalyst bed. Water is circulated in these tubes and steam is thereby generated directly without the need of a secondary heat-transfer fluid.

The conversion of naphthalene in the reactor is 100% with a yield of 0.97 kg phthalic anhydride per kilogram of naphthalene feed.[35] (The theoretical yield is 1.16 kg per kilogram of 100% naphthalene.[1])

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[34] Graham, J. J. The Fluidized Bed Phthalic Anhydride Process. Chemical Engineering Progress. 66:54-58, September 1970.

[35] Phthalic Anhydride (Sherwin-Williams/Badger). The Badger Company, Inc. Hydrocarbon Processing. 46:215, November 1967.

d. Catalyst Filter - Effluent gases leaving the reactor are cooled to about 260°C before entering the catalyst filter unit (unit E) in order to prevent secondary reactions taking place on the filters.[a] The entrained catalyst particles are separated from the gas stream by specially designed porous ceramic filter elements. Process air is used to periodically blow back the filters, and the catalyst particles are returned directly to the reactor bed. Fiber glass filters, used in some processes, are described in detail in Reference 12.

e. Condensers - Due to the low air to naphthalene ratio employed in the fluid-bed process, the crude phthalic anhydride is recovered both as a liquid and a solid. Between 40% and 60%[29] of the product is obtained directly as a liquid in the partial condenser (unit G) and the remainder is condensed as a solid in the switch condensers (units H). The latter operate in the same manner as those described for the BASF process. However, the partial condensation of product plus the reduced air rate greatly reduces the load on the switch condensers with a concomitant reduction in size and cost.

The tail gases (stream 8) leave the switch condensers at 66°C and are sent either to a water scrubber (unit J) or directly to the incinerator (unit K). The low air rate

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[a] The cooling may be accomplished in a quenching section within the reactor itself, rather than in an external heat exchanger as shown in Figure 5. The quenching section is simply a second fluidized bed located above the main bed and separated from it by a grid plate. Further details of this reactor scheme may be found in Reference 36.

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[36] Rousseau, W. P. C. Production of Phthalic Anhydride. U.S. Patent No. 3,080,382 (to the Badger Co.), March 5, 1963.

makes direct incineration more economical than in the fixed-bed process.

The crude product is stored as a liquid at 149°C and atmospheric pressure (unit I).

f. Product Purification - Crude phthalic anhydride (stream 12) from the crude product storage tank passes through a preheater (unit L) and then to the pretreatment tank (unit M) in much the same manner as in the BASF process. Treating chemicals consisting of maleic anhydride (1 g per kilogram PAN) and sodium hydroxide (0.05 g per kilogram PAN) are added to promote the pretreatment process.[37] In the Badger-Sherwin-Williams process the final product is obtained by means of a batch distillation column which operates at an absolute pressure of 2.66 kPa. The light ends (stream 16) are taken off at a reflux ratio of 40 and sent to the incinerator for disposal. The main cut is then taken at a reflux ratio of 1, condensed, and sent to the phthalic anhydride storage tank (unit P), where it is held at 149°C and atmospheric pressure. The residue, or bottoms product, is sent to the incinerator.

The refined phthalic anhydride (99.7% minimum) can be pumped to tank cars for shipment in liquid form, or it can be sent to flaking and bagging machines (units Q and R) for shipment as a solid.

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[37] Personal communication, L. B. Evans, U.S. Environmental Protection Agency (Data originally supplied by Union Carbide Corporation). June 12, 1975.

g. Scrubber and Incinerator -

(1) Scrubber - The characteristics of the effluent gas from the switch condensers impose a number of constraints on the design of a scrubber for phthalic anhydride plants:

- The efficient removal of aldehydes and maleic anhydride requires a multistage rather than a single-stage unit.[14,38]
- Since the liquid effluent from the scrubber must be incinerated to avoid a water pollution problem, a recycle system is necessary to minimize the volume of the effluent stream.
- The organic compounds present in the condenser tail gas are highly corrosive, thus requiring the use of corrosion resistant materials of construction.

A scrubber designed to meet the above requirements is illustrated in Figure 6.[38] (The process streams in Figure 6 are numbered for later reference to the material balance given in Table 11.) The unit consists of two stages, each of which contains a conventional fluid-bed packing on a supporting grid. The two stages are separated by a conical shaped deflector plate and collection tray. The unit is designed to operate between 35°C and 40°C with an organic removal efficiency of 98% to 99%. This high efficiency is possible because most of the organics are solids at the scrubber operating conditions. The material of construction is 316 stainless steel.

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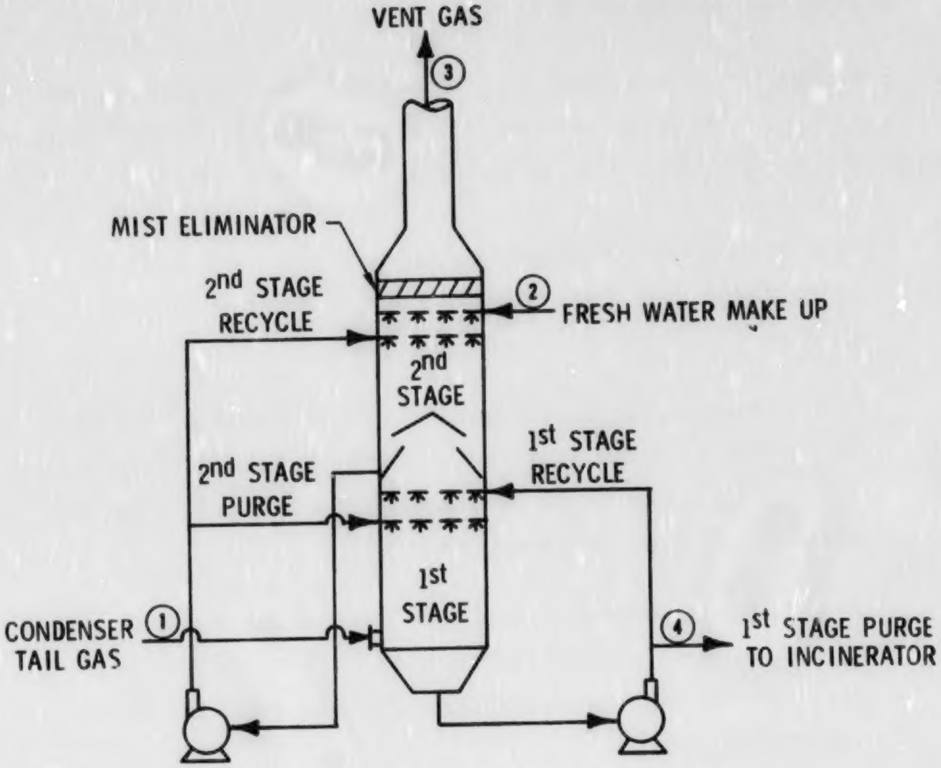
[38] Ferrari, D. C., and C. G. Bertram. Method and Apparatus for the Removal of Organics from Chemical Waste Gases. U.S. Patent No. 3,624,984 (to the Badger Co.), December 7, 1971.



VENT GAS
③
MIST ELIMINATOR
2nd STAGE RECYCLE
②
FRESH WATER MAKE UP
2nd STAGE
1st STAGE RECYCLE
2nd STAGE PURGE
1st STAGE
CONDENSER TAIL GAS
①
④
1st STAGE PURGE TO INCINERATOR

Figure 6. Schematic diagram of scrubber for phthalic anhydride plant[38]

The condenser tail gas enters the first stage at approximately 66°C. The scrubbing liquor for this stage consists of the purge from the second stage and the first stage recycle stream. The liquor is slurry containing 10% to 12% by weight of organic solids. The concentration of organic compounds, both dissolved and in the form of slurry solids, ranges from 10% to 50% by weight depending on the composition of the gas being treated. A portion of the recycle stream is continuously purged and sent to the incinerator for disposal.

In the second stage, the gas is scrubbed with a dilute solution (0.5% to 3% by weight) of organic pollutants (chiefly maleic acid). Fresh water is added to the second stage at a rate sufficient to replace the water removed from the scrubber in the two exit streams. The makeup water combines with the second stage recycle stream to form the second stage scrubbing liquor. The scrubbed gas stream passes through a mist eliminator and is then vented to the atmosphere at 38°C.

Table 11 gives a typical scrubber material balance, obtained from the Badger patent,[38] for a naphthalene based phthalic anhydride operation. In this example, only the condenser effluent stream is fed to the scrubber. In practice, the exhaust gases from the steam ejectors in the purification section of the phthalic anhydride plant may also be fed to the scrubber. In addition, it will be noted that sulfur

Table 11. TYPICAL SCRUBBER MATERIAL BALANCE FOR A NAPHTHALENE BASED PHTHALIC ANHYDRIDE PLANT[a]

Stream No.:	1	2	3	4
Description:	Condenser tail gas	Makeup water	Vent gas	1st stage purge
Temperature, °C:	66	16	38	38
Component	Flow rates, kg/hr			
Air	222,273		222,273	
H_2O	4,545	6,272	9,545	1,202
Maleic anhydride	291		4.6	
Phthalic anhydride	141		2.3	
Benzoic acid	11		0.5	11
Naphthoquinone	11		0.9	11
Maleic acid				339
Phthalic acid				155
TOTALS	227,272	6,272	231,826	1,718

[a] Blanks indicate no mass flow of component

and carbon oxides are included with the air, since they behave as inert gases in the scrubbing operation. The flow rates in this example correspond to a production rate of approximately 5.68 x 10^4 metric tons/yr.

(2) Incinerator - Incinerators used in phthalic anhydride plants are of two types: direct flame (thermal) units and catalytic units. Catalytic incinerators are auto-thermal and operate at temperatures of 427°C to 482°C. The catalyst is platinum, platinum family or platinum activated alumina on a metal ribbon mesh or ceramic base.[14] Thermal incinerators operate at temperatures of 700°C to 982°C and consume fuel equivalent to 279 kJ per kilogram of phthalic anhydride produced.[38]

A thermal incinerator[38] is shown schematically in Figure 7. (The process streams in Figure 7 are numbered for later reference to the material balance given in Table 13.) The primary feed stream to the incinerator is the liquid purge from the first stage of the scrubber. Other feed streams may include the residue (liquid), light ends (gas), and ejector exhaust (gas) streams from the product purification section of the plant. Heating values of the main organic components in the scrubber purge stream are listed in Table 12. The heating value of the liquid residue stream is estimated to be 23.3 MJ/kg.[38]

Table 12. HEATING VALUES OF ORGANIC COMPOUNDS IN SCRUBBER PURGE STREAM

Compound	Gross heat of combustion, MJ/kg
Maleic acid	13.8
Phthalic acid	21.6
Benzoic acid	26.5
Naphthoquinone	29.1

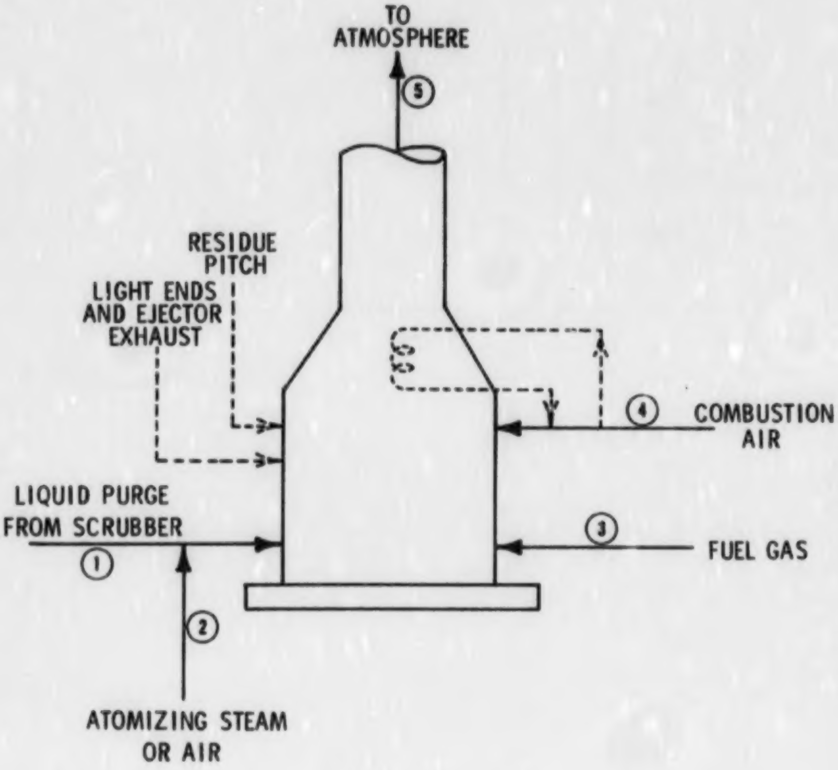

TO ATMOSPHERE
⑤
RESIDUE PITCH
LIGHT ENDS AND EJECTOR EXHAUST
④
COMBUSTION AIR
LIQUID PURGE FROM SCRUBBER
①
③
FUEL GAS
②
ATOMIZING STEAM OR AIR

Figure 7. Schematic diagram of thermal incinerator for phthalic anhydride plant[38]

The liquid purge stream is atomized immediately before entering the combustion area of the incinerator by either a steam or an air stream. Fuel gas (e.g., methane) and combustion air (25% in excess of the stoichiometric amount) are introduced into the incinerator in a conventional manner to provide an operating temperature of 760°C to 870°C. Heat recovery is achieved by means of a coil which can be used either to preheat the combustion air (as shown in Figure 6) or to generate steam.

The incinerator reportedly attains an efficiency of 99.9% conversion of organic materials. A material balance on the incinerator[38] is shown in Table 13. The feed stream in this example is the scrubber purge stream of Table 11.

Table 13. INCINERATOR MATERIAL BALANCE FOR A NAPHTHALENE BASED PHTHALIC ANHYDRIDE PLANT[a]

Stream No.:	1	2	3	4	5
Description:	Scrubber purge	Atomizing steam	Fuel gas	Combustion air	Stack gas
Temperature, °C:	38	186	16	16	760
Component	Flow rates, kg/hr				
Maleic acid	339				
Phthalic acid	155				
Benzoic acid	11				
Naphthoquinone	11				
H_2O	1,202	572			2,006
Oxygen				823	155
Nitrogen				2,717	2,717
Methane			30		
CO_2					982
Organics					0.0059
TOTAL	1,718	572	30	3,540	5,860

[a] Blanks indicate no mass flow of component.

h. Storage Tanks - Table 14 summarizes the feedstock, crude product, and refined product storage tank requirements for a 5.9 x 10^4 metric tons/yr naphthalene based phthalic anhydride plant.[30] The crude and refined phthalic anhydride is stored under the same conditions as described previously for *o*-xylene based plants. Naphthalene storage tanks are maintained at 85°C to 100°C, at which temperatures the vapor pressure is 1.33 kPa to 2.67 kPa. Emission of naphthalene vapor can be controlled by means of conservation vents.

Table 14. SUMMARY OF TANKAGE REQUIREMENTS FOR A 5.9 x 10^4 METRIC TONS/YR NAPHTHALENE BASED PHTHALIC ANHYDRIDE PLANT

Tank no.	Material stored	Capacity, m^3	Turnovers per year
1	Naphthalene	3,785	1
2	Naphthalene	3,785	13
3	Naphthalene	1,893	26
4	Crude product	333	148
5	Crude product	1,514	2
6	Phthalic anhydride	182	130
7	Phthalic anhydride	182	130
8	Phthalic anhydride	568	2
9	Phthalic anhydride	568	40

i. Catalyst Storage Facilities - The fluid-bed process involves two catalyst storage facilities which are not shown in Figure 5. During the blow-back cycle of the catalyst filter (unit E), the fines fraction of the fluid-bed catalyst is separated and removed from the system as "spent" catalyst. The fines fraction consists primarily of catalyst particles less than 40 μm in diameter. The spent catalyst stream is sent to a tangential cyclonic separator where the catalyst particles are removed from the entraining air stream with a removal efficiency of 98.5%.[37] The recovered catalyst flows by gravity to a drum, approximately 0.2 m^3 in volume, which is designated the spent catalyst storage facility. The exhaust gas stream from the cyclone is vented to the atmosphere. This operation is intermittent and totals approximately 50 hr/yr.[37]

During periods of reactor shutdown for routine or emergency maintenance, the catalyst is removed from the reactor and transferred pneumatically to a catalyst storage hopper. This operation is performed an average of four to eight times per year, and has a duration of about 12 hours.[37]

The hopper vent is equipped with a cyclone separator that recovers entrained catalyst with an efficiency of 90%.[37] The recovered catalyst is returned to the storage hopper, while the exhaust gas stream from the cyclone vents to the atmosphere.

j. Heat Transfer Circuits - The Badger-Sherwin-Williams process employs two organic fluid heat-transfer systems: (1) the circuit that heats and cools the switch condensers (units H); and (2) the circuit which services the product purification train (units L, M, N, O). The fluid-bed reactor is water cooled (units D and F). The organic fluid systems are similar to those discussed previously for the BASF process (Section III.A.1.h.).

k. Plant Shutdown, Turnaround, and Start-up - Naphthalene based phthalic anhydride plants are shut down for emergency or routine maintenance an average of four to eight times per year.[37] During these periods, the fluid-bed catalyst is transferred pneumatically from the reactor to the catalyst storage hopper as described above. These transfer operations result in emissions of catalyst particles from the storage hopper vent and from fugitive sources. No data are available on emissions of heat-transfer fluid (designated "oil" in Figure 5) from the heating and cooling circuits during start-up and other process upset conditions. However, these emissions are presumably similar to those experienced by o-xylene based plants, which have been described previously.

1. Catalyst - Davison Grade 902 Catalyst[a] is a finely divided vanadium oxide catalyst on a silica gel base used for the direct air oxidation of naphthalene to phthalic anhydride in fluid-bed reactors. Typical chemical and physical specifications are given in Table 15.

Table 15. TYPICAL PROPERTIES OF DAVISON GRADE 902 CATALYST

Chemical analysis	Wt %
Volatile at 374°C	1
V_2O_5	9
K_2SO_4	29
SO_3	12
SiO_2	50
Physical analysis	**Value**
Bulk density	195 kg/m^3
Surface area	40 m^2/g
Average pore diameter	3 mm
Particle size distribution	**Wt %**
≤20 μm	12
>20 μm but ≤40 μm	11
>40 μm but ≤80 μm	28
>80 μm	49

---

[a] W. R. Grace & Company, Davison Chemical Division. A newer version of this catalyst, Davison Grade 906, is reported in Reference 37. Grade 906 contains 3.5% V_2O_5 by weight.

The primary purpose of the K_2SO_4 modifier is to slow down the reaction rate and prevent over-oxidation of the naphthalene.[29] The Badger-Sherwin-Williams reactor uses 0.6 gram of catalyst per kilogram of phthalic anhydride produced.[37]

m. Reactor System Heat Balance - The oxidation of naphthalene is an exothermic chemical reaction. The standard heats of reaction for the main reaction and principal side reactions were calculated on the basis that all of the compounds involved are in the vapor state, and the results are listed in Table 16. Published figures for the heat released in a commercial reactor are 16.3 to 20.9 MJ/kg phthalic anhydride.[9] A value of 17 MJ/kg phthalic anhydride was estimated in Reference 26, and is in good agreement with an estimate based on the data in Table 16.

Table 16. HEATS OF REACTION FOR THE OXIDATION OF NAPHTHALENE

Reaction	Heat of reaction	
	MJ/kg	MJ/kg mol
Naphthalene + $4.5O_2$ → phthalic anhydride + $2CO_2$ + $2H_2O$	14.0	2,732
Naphthalene + $9O_2$ → maleic anhydride + $6CO_2$ + $3H_2O$	28.4	395
Naphthalene + $1.5O_2$ → naphthoquinone + H_2O	3.7	51
Naphthalene + $12O_2$ → $10CO_2$ + $4H_2O$	39.6	547

Steam is generated by circulating water through the reactor cooling coils, and also in the partial condenser. Part of this steam is used to satisfy process requirements and the remainder is available for export. A representative energy balance for a naphthalene based phthalic anhydride plant is presented in Table 17.

Table 17. REACTOR SYSTEM HEAT BALANCE FOR PRODUCTION OF PHTHALIC ANHYDRIDE FROM NAPHTHALENE[a]

Heat in	MJ/kg PAN
Exothermic heat of reaction	17.0
Air preheat	1.5
Total	18.5
Heat out	**MJ/kg PAN**
Steam generation	
Reactor internal cooling	13.2
Partial condenser	2.0
Reactor heat loss	0.1
Reactor effluent cooler	1.6
Switch condensers	1.2
Incremental effluent heat content[b]	0.4
Total	18.5

[a] Basis:
Material balance given in Table 19.
Naphthalene feed at 93°C, air at 26.7°C.
Air preheated to 149°C.
Reactor outlet temperature, 371°C.
Condenser effluent gas at 66°C.

[b] Difference in heat content between condenser effluent streams and reactor feed streams.

B. MATERIALS FLOW

1. o-Xylene Based Process

The flow diagram for the BASF process was given in Figure 2. Table 18 is a material balance for a typical 5.9 x 10^4 metric tons/yr plant, based on data obtained from Reference 26.

Table 18. MATERIAL BALANCE FOR A 5.9 x 10^4 METRIC TONS/YR o-XYLENE BASED PHTHALIC ANHYDRIDE PLANT

Stream No.:	1	2	3	4	5	6	7	8
Description:	Xylene	Sulfur dioxide	Air	Reactor feed	Reactor product	Boiler effluent	Crude product	Condenser off-gas
Temperature, °C:	27	27	27	149	375	163	149	66
Gage pressure, kPa:[a]	0		0	50			0	26
Component	Flow rates,[b] kg/hr							
Sulfur dioxide		34.1		34.1	34.1	34.1		34.1
Carbon monoxide					1,095.9	1,095.9		1,095.9
Carbon dioxide					3,784.6	3,784.6		3,784.6
Nitrogen			140,897.3	140,897.3	140,897.3	140,897.3	34.5	140,862.8
Oxygen			42,804.1	42,804.1	32,819.1	32,819.1		32,819.1
Phthalic anhydride					7,517.7	7,517.7	7,350.4	167.3
Maleic anhydride					591.8	591.8	276.4	315.4
Benzoic acid					51.8	51.8	31.4	20.4
o-Xylene	7,098.6			7,098.6				
m- and p-Xylene	334.6			334.6				
Misc. organics[c]					34.1	34.1	34.1	
Particulate								
Water			1,996.8	1,996.8	6,339.1	6,339.1		6,339.1
Total	7,433.2	34.1	185,698.2	193,165.5	193,165.5	193,165.5	7,726.8	185,438.7

[a] Blanks indicate data not available.

[b] Blanks indicate no mass flow of exponent.

[c] Listed in Table 21.

Table 18 (continued). MATERIAL BALANCE FOR A 5.9 x 10^4 METRIC TONS/YR o-XYLENE BASED PHTHALIC ANHYDRIDE PLANT

Stream No.:	9	10	11	12	13	14	15	16
Description:	Scrubber vent	Scrubber liq. purge	Crude PAN	Pretreatment exhaust	Pretreated crude	Stripping col. exhaust	Stripping col. overhead	Rectifying col. feed
Temperature, °C:[a]	38	38	149					186
Gage pressure, kPa:[a]	0		0	-98.6		-98.6	-98.6	
Component	Flow rates,[b] kg/hr							
Sulfur dioxide	34.1							
Carbon monoxide	1,095.9							
Carbon dioxide	3,784.6							
Nitrogen	140,897.3		34.5	34.5				
Oxygen	32,819.1							
Phthalic anhydride	3.2	193.6	7,350.4	31.8	7,318.6			7,280.0
Maleic anhydride	8.2	321.8	276.4	14.6	261.8			14.5
Benzoic acid	6.8	13.6	31.4		31.4			
o-Xylene								
m- and p-Xylene								
Misc. organics								
Particulate	4.6[d]		34.1		34.1			34.1
Water	7,680.9	3,866.8		2,181.8[e]				
Total	186,334.7	4,395.8	7,726.8	2,262.7	7,645.9			7,328.6

[a] Blanks indicate data not available.

[b] Blanks indicate no mass flow of component.

[d] Primarily solids from make-up water.

[e] 2181.8 kg/hr H_2O condensate from steam ejector.

Table 18 (continued). MATERIAL BALANCE FOR A 5.9 x 10^4 METRIC TONS/YR o-XYLENE BASED PHTHALIC ANHYDRIDE PLANT

Stream No.:	17	18	19	20	21	22	23	24
Description:	Rectifying column vac. exhaust	Rectifying col. bottom product	Distillation light Ends	Refined PAN	Water to steam gen.	Generated steam	Water to waste-ht. boiler	Steam from waste-ht. boiler
Temperature, °C:[a]				149	16	213	16	157
Gage pressure, kPa:[a]	-98.6			0		1,910		476
Component	Flow rates,[b] kg/hr							
Sulfur dioxide								
Carbon monoxide								
Carbon dioxide								
Nitrogen								
Oxygen								
Phthalic anhydride		7.3	38.6	7,272.7				
Maleic anhydride			247.3	14.6				
Benzoic acid			31.4					
o-Xylene								
m- and p-Xylene								
Misc. organics[c]		34.1						
Particulate								
Water					28,527.3	28,527.3	16,263.6	16,263.6
Total		41.4	317.3	7,287.3	28,527.3	28,527.3	16,263.6	16,263.6

[a] Blanks indicate data not available.

[b] Blanks indicate no mass flow of component.

[c] Listed in Table 21.

Table 18 (continued). MATERIAL BALANCE FOR A 5.9 x 10^4 METRIC TONS/YR o-XYLENE BASED PHTHALIC ANHYDRIDE PLANT

Stream No.:	25	26	27	28	29	30	31	32
Description:	Scrubber makeup	Incinerator stack gas	Water to cooling coil	Steam from cooling coil	Water to cooling coil	Steam from cooling coil	Incinerator fuel	Combustion Air
Temperature, °C:[a]	16	927	16	129	16	129	16	27
Gage pressure, kPa:		0		160		160		0
Component	Flow rates,[b] kg/hr							
Sulfur dioxide								
Carbon monoxide		18.2						
Carbon dioxide		2,759.1						
Nitrogen		9,660.9					30.5	9,630.9
Oxygen		395.4						2,916.8
Phthalic anhydride								
Maleic anhydride								
Benzoic acid		3.6						
o-Xylene								
m- and p-Xylene								
Misc. organics								
Particulate		3.2[f]						
Water	3,026.8	4,992.3						136.4
Ethane							65.9	
Methane							299.1	
Nitrogen oxides		1.4						
Total	3,026.8	17,834.1	—	—	—	—	395.5	12,684.1

[a] Blanks indicate data not available.

[b] Blanks indicate no mass flow of component.

[f] Primarily solids from make-up water.

Table 18 (continued). MATERIAL BALANCE FOR A 5.9 x 10^4 METRIC TONS/YR o-XYLENE BASED PHTHALIC ANHYDRIDE PLANT

Stream No.:	33	34	35	36	37	38
Description:	Flaker and bagger vent	o-Xylene stg. vent	Crude product stg. vent	PAN stg. vent	Loading facility vent	Fugitive emissions
Temperature, °C:	27	27	149	149	27	27
Gage pressure, kPa	0	0	0	0	0	0
Component	Flow rates,[b] kg/hr					
Sulfur dioxide						
Carbon monoxide						
Carbon dioxide						
Nitrogen						
Oxygen						
Phthalic anhydride	0.007		0.008	0.02	0.03	
Maleic anhydride						
Benzoic acid						
o-Xylene		0.014				
m- and p-Xylene						
Misc. organics						
Particulate						
Water						
Total	0.007	0.014	0.008	0.02	0.03	

[b] Blanks indicate no mass flow of component.

Sources of atmospheric emissions from the BASF.process are: the scrubber vent (stream 9) and/or the incinerator flue gas (stream 26), xylene storage (stream 34), crude product storage (stream 35), refined product storage (stream 36), flaker and bagger vent (stream 33), transport loading facility vent (stream 37), and fugitive emissions (stream 38). In addition, plants which employ a secondary scrubber or incinerator to control waste streams from the product purification section of the plant will have emissions from these devices.

2. Naphthalene Based Process

The flow diagram for the Badger-Sherwin-Williams process was given in Figure 5. Table 19 is a material balance for a 5.9×10^4 metric tons/yr plant, based on data obtained from Reference 26.

Sources of atmospheric emissions from the Badger-Sherwin-Williams process are: the scrubber vent (stream 9), and/or the incinerator flue gas (stream 19), naphthalene storage (stream 27), crude product storage (stream 28), refined product storage (stream 29), flaker and bagger vent (stream 26), transport loading facility vent (stream 31), catalyst storage hopper vents (stream 30), and fugitive emissions (stream 32).

C. GEOGRAPHICAL DISTRIBUTION

There are currently eight companies manufacturing phthalic anhydride at ten locations in the continental United States, plus one in Puerto Rico. Table 20 lists the manufacturers and plant capacities, and the plant locations are shown in Figure 8. The population densities of the counties in which the plants are located range from 30 to 4,905 persons/km^2.

Table 19. MATERIAL BALANCE FOR A 5.9 x 10^4 METRIC TONS/YR NAPHTHALENE BASED PHTHALIC ANHYDRIDE PLANT

Stream No.:	1	2	3	4	5	6	7	8
Description:	Naphthalene	Air	Reactor product	Crude from partial condenser	Part. cond. off-gas	Crude from switch cond.	Crude product	Switch-cond. off-gas
Temperature, °C:[a]	93	27	260	149		149	149	66
Gage pressure, kPa:[a]	0	0					0	
Component	Flow rates,[b] kg/hr							
Naphthalene	7,497.3							
Phthalic anhydride			7,492.3				7,344.1	148.2
Maleic anhydride			101.4				50.4	50.9
Naphthoquinone			53.2				48.2	5.0
Misc. organics	37.7		37.7				37.7	
Oxygen		22,130.0	12,225.4				17.3	12,208.2
Nitrogen		68,197.3	68,197.3				20.0	68,177.3
Carbon dioxide			7,030.4					7,030.4
Carbon monoxide			366.4					366.4
Water			2,356.4				65.5	2,290.9
Total	7,535.0	90,327.3	97,860.5				7,583.2	90,277.3

[a] Blanks indicate data not available.

[b] Blanks indicate no mass flow of component.

Table 19 (continued). MATERIAL BALANCE FOR A 5.9 x 10^4 METRIC TONS/YR NAPHTHALENE BASED PHTHALIC ANHYDRIDE PLANT

Stream No.:	9	10	11	12	13	14	15	16
Description:	Scrubber vent	Scrubber makeup	Scrubber liq. purge	Crude PAN	Pretreatment vac. exhaust	Dist. col. feed	Dist. col. vac. exhaust	Dist. col. light ends
Temperature, °C:[a]	38	16	38	149		186		
Gage pressure, kPa:[a]	0			0	-98.6		-98.6	-98.6
Component	Flow rates,[b] kg/hr							
Naphthalene								
Phthalic anhydride				7,344.1	18.2			
Maleic anhydride				50.4				5.0
Naphthoquinone				48.2				35.9
Misc. organics				37.7				
Oxygen	12,208.2			17.3	17.3			
Nitrogen	68,177.3			20.0	20.0			
Carbon dioxide	7,030.4							
Carbon monoxide	366.4							
Water				65.5	65.5			
Total				7,583.2	121.0			40.9

[a] Blanks indicate data not available.

[b] Blanks indicate no mass flow of component.

Table 19 (continued). MATERIAL BALANCE FOR A 5.9 x 10^4 METRIC TONS/YR NAPHTHALENE BASED PHTHALIC ANHYDRIDE PLANT

Stream No.:	17	18	19	20	21	22	23	24
Description:	Dist. col. bottom prod.	Refined PAN	Incinerator stack gas	Incinerator fuel	Combustion air	Water to steam gen.	Steam from steam gen.	Cooling water
Temperature, °C:[a]		149	927	16	27	16	213	16
Gage pressure, kPa:[a]		0	0		0		1,910	
Component	Flow rates,[b] kg/hr							
Naphthalene								
Phthalic anhydride	48.2	7,272.7						
Maleic anhydride		14.6						
Naphthoquinone	48.2							
Misc. organics	37.7							
Oxygen								
Nitrogen								
Carbon dioxide								
Carbon monoxide								
Water						35,154.6	35,154.6	5,340.9
Methane								
Ethane								
Particulate								
Nitrogen oxides								
Total	134.1	7,287.3				35,154.6	35,154.6	5,340.9

[a] Blanks indicate data not available.

[b] Blanks indicate no mass flow of component.

Table 19 (continued). MATERIAL BALANCE FOR A 5.9 x 10^4 METRIC TONS/YR NAPHTHALENE BASED PHTHALIC ANHYDRIDE PLANT

Stream No.:	25	26	27	28	29	30	31	32
Description:	Steam	Flaker and bagger vent	Naphthalene stg. vent	Crude prod. stg. vent	PAN stg. vent	Catalyst storage hopper vents	Loading facility vent	Fugitive emissions
Temperature, °C:	135	27	90	149	149	27	27	27
Gage pressure, kPa:	207	0	0	0	0	0	0	0
Component	Flow rates,[b] kg/hr							
Naphthalene			0.044					
Phthalic anhydride		0.007		0.012	0.014		0.03	
Maleic anhydride								
Naphthoquinone								
Misc. organics								
Oxygen								
Nitrogen								
Carbon dioxide								
Carbon monoxide								
Water	5,340.9							
Total	5,340.9	0.007	0.044	0.012	0.014		0.03	

[b] Blanks indicate no mass flow of component.

Table 20. PHTHALIC ANHYDRIDE PLANTS[3,4]

Number[a]	Company	Nominal capacity, 10^3 metric tons/yr	Location	County population density, persons/km^2	Raw material	Process
1	Allied Chemical	15.9	El Segundo, Calif.	662	o-Xylene	Chemiebau (von Heyden)
2	BASF Wyandotte	59.0	S. Kearny, N.J.	4,905	o-Xylene	BASF
3	Exxon Corp.	40.8	Baton Rouge, La.	233	o-Xylene	BASF
4	Koppers Co.	40.8	Bridgeville, Pa.	842	Desulf. naphthalene	Own (fluid bed)
5	Koppers Co.	79.4	Cicero, Ill.	2,197	o-Xylene	BASF
6	Monsanto Co.	40.8	Bridgeport, N.J.	64	Petro naphthalene	Badger-Sherwin-Williams
7	Monsanto Co.	59.0	Texas City, Texas	160	o-Xylene	BASF
8	Std. Oil Calif.	22.7	Richmond, Calif.	152	o-Xylene	Lurgi (von Heyden)
9	Stepan Chem. Co.	22.7	Millsdale, Ill.	112	o-Xylene	Chemiebau (von Heyden)
10	U.S. Steel	68.0	Neville Island, Pa.	30	Desulf. naphthalene	Badger-Sherwin-Williams
--	Occidental Petroleum	45.4	Arecibo, P.R.	39	o-Xylene	Chemiebau (von Heyden)
			The following plants are not in operation:			
--	Union Carbide Co.	45.4	Institute and South Charleston, W. Va.	95	Petro naphthalene	Badger-Sherwin-Williams
--	Allied Chemical	45.4	Frankford, Pa.	5,861	Naphthalene	Badger
--	Allied Chemical	15.0	Ironton, Ohio	47	Naphthalene	Own (fixed bed)
--	W. R. Grace	34.0	Fords, N.J.	714	Naphthalene	Badger-Sherwin-Williams
--	Reichhold Chemicals	13.6	Elizabeth, N.J.	2,020	Naphthalene	Badger-Sherwin-Williams
--	Reichhold Chemicals	45.4	Morris, Ill.	22	o-Xylene	Unknown
--	Sherwin-Williams	9.1	Chicago, Ill.	2,197	Naphthalene	Badger-Sherwin-Williams

[a] Numbers refer to code shown in Figure 8.

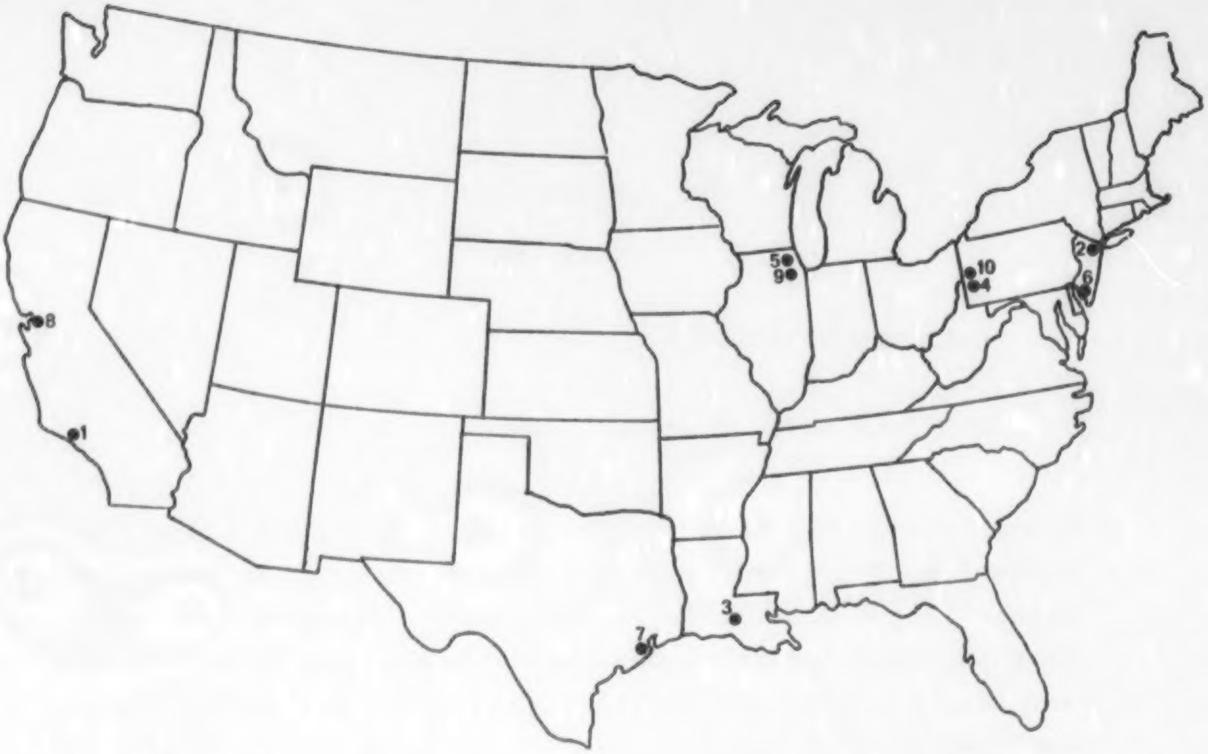


Figure 8. Phthalic anhydride plant locations

The total U.S. capacity in 1975 was 4.95 x 10^5 metric tons/yr. In addition to this, a 2.27 x 10^4 metric tons/yr expansion of the U.S. Steel Plant at Neville Island, Pennsylvania is scheduled for completion in 1975.[4]

SECTION IV

EMISSIONS

A. SELECTED POLLUTANTS

1. o-Xylene Based Process

A complete list of the possible reaction products from the oxidation of xylene, according to the work of Bernardini and Ramacci,[5] and Bhattacharyya and Gulati,[7] is given in Table 21. In these experimental laboratory studies, gas chromatography and various other quantitative analytical techniques were employed to identify the reaction products. In addition to the compounds shown in Table 21, emissions from o-xylene based phthalic anhydride plants contain sulfur oxides, nitrogen oxides, particulates, and diphenyl oxide (from Dowtherm® heat-transfer fluid). Of the above mentioned compounds, the following are either known or suspected of being emitted on the basis of previously published data:[14,26] o-xylene, phthalic anhydride, maleic anhydride, benzoic acid, o-tolualdehyde, formaldehyde, acetaldehyde, phthalaldehyde, acrolein, carbon monoxide, sulfur oxides, nitrogen oxides, particulates, and diphenyl oxide. Hence, these compounds were selected for study in this program. The rationale for not considering the remaining materials listed in Table 21 is presented in Appendix B.

Table 21. POSSIBLE REACTION PRODUCTS FROM THE OXIDATION OF XYLENE

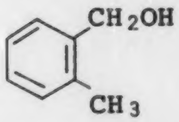
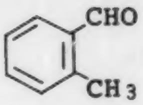
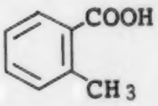
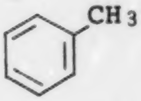
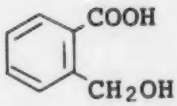
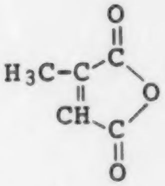
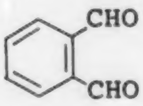
Compound	Formula
o-Methylbenzyl alcohol	
o-Tolualdehyde	
o-Toluic acid	
Toluene	
o-Hydroxymethylbenzoic acid	
Citraconic anhydride	
Phthalaldehyde	

Table 21 (continued). POSSIBLE REACTION PRODUCTS FROM THE OXIDATION OF XYLENE

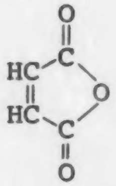
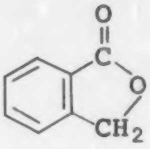
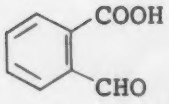
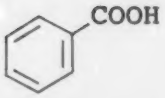
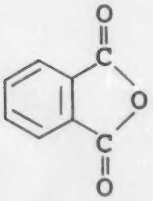
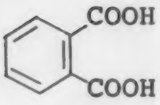
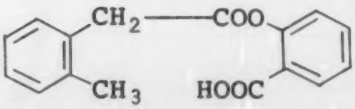
Compound	Formula
Maleic anhydride	
Phthalide	
Phthalaldehydic acid	
Benzoic acid	
Phthalic anhydride	
Phthalic acid	
Carbon oxides and water	CO, CO_2, H_2O
o'-Carboxylphenyl-o-methylphenyl acetate	

Table 21 (continued). POSSIBLE REACTION PRODUCTS FROM THE OXIDATION OF XYLENE

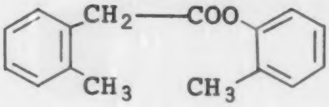
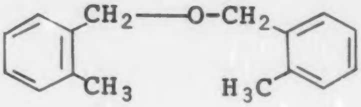
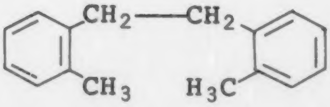
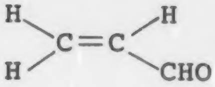
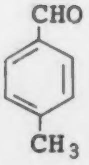
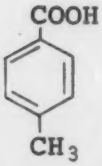
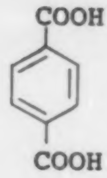
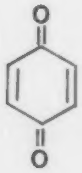
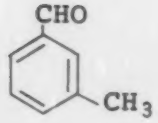
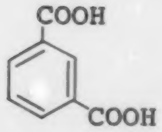
Compound	Formula
o'-Methylphenyl-o-methylphenyl acetate	
bis(*o*-Methylphenyl) methyl ether	
1,2-bis(*o*-Methylphenyl) ethane	
Formaldehyde	HCHO
Acetaldehyde	CH_3CHO
Acrolein	
p-Tolualdehyde	
p-Toluic acid	

Table 21 (continued). POSSIBLE REACTION PRODUCTS FROM THE OXIDATION OF XYLENE

Compound	Formula
Terephthalic acid	
p-Benzoquinone	
m-Tolualdehyde	
Isophthalic acid	

2. Naphthalene Based Process

A reaction scheme for the oxidation of naphthalene, similar to that for the oxidation of o-xylene, has not been published. In addition to the reaction sequence given in Section III.A.2.b. involving 1,4-naphthoquinone, Shelstad, et al.,[28] have reported a path involving 1,2-napththoquinone as an intermediate. Thus, 1,2-dihydroxynaphthalene and 1,2-naphthoquinone are expected reaction products. In addition, the compounds listed in Table 21 may also be formed by the oxidation of naphthalene. Furthermore, transfer operations involving the fluid-bed catalyst result in emissions of vanadium oxide catalyst dust. Hence, the species selected for detailed study in this program include those selected for the o-xylene based process, with the addition of naphthalene, the naphthoquinones, the dihydroxynaphthalenes, and vanadium oxide catalyst dust.

B. LOCATION AND DESCRIPTION

The sources of atmospheric emissions within phthalic anhydride plants are: the main process scrubber vent and/or the incinerator stack, storage tank vents (feedstock, crude product, and refined product), the flaker and bagger vent, the liquid product loading facility vent, and fugitive emissions. The catalyst storage hopper vents are an additional source of emissions in naphthalene based plants. Those plants which employ a secondary scrubber or incinerator to treat the waste streams from the product purification section of the plant also have emissions from these units. Each of the above sources is discussed below.

1. Scrubber Vent

The scrubber vent gas (stream 9 in Figures 2 and 5) is a continuous source of emissions consisting of scrubbed process off-gas from the switch condensers. Typical concentration ranges for the major contaminants in the condenser off-gas, as given by Fawcett,[14] are shown in

Table 22. The corresponding flow rates for a 5.9 x 10^4 metric tons/yr plant are in agreement with the material balances given in Tables 18 and 19 (which are based on the Houdry data[26]) with one exception: that is, the flow rate of maleic anhydride for a naphthalene based plant, which is 51 kg/hr in Table 19.

The organic compounds are removed from the condenser off-gas stream with a maximum efficiency of 98% to 99% in the scrubber,[38] while the carbon and sulfur oxides are vented to the atmosphere. Typical compositions for the scrubber vent gas stream are presented in Tables 23 and 24 for o-xylene and naphthalene based plants, respectively. These values are based on the material balance data of Tables 18 and 19 and, in the case of naphthalene based plants, the assumption of a scrubber efficiency of 98% for organics.

2. Incinerator Stack

The incinerator flue gas (stream 26 in Figure 2 and stream 19 in Figure 5) is another continuous source of emissions. The incinerator is used to burn the liquid purge from the scrubber or, in the case of plants employing direct incineration, the switch-condenser off-gas. The waste streams from the product purification section of the plant and the phthalic anhydride storage tank vents may also be fed to the incinerator. Typical compositions of the stack gas are presented in Tables 25 and 26 for o-xylene and naphthalene based plants employing a scrubber-incinerator combination. These values are based on the material balances given in Tables 18 and 19 and, in the case of naphthalene based plants, on the assumption of organic removal efficiencies of 98% and 99% in the scrubber and incinerator, respectively. The results for plants

Table 22. CONCENTRATIONS OF CONTAMINANTS IN SWITCH-CONDENSER OFF-GAS[14]

Material	Concentration, ppm by vol.	Flow rate,[a] kg/hr	Uncontrolled emission factor, g/kg
Phthalic anhydride	40-200	39-193	5.4-26.5
Maleic anhydride	100-600	64-383	8.8-52.6
Benzoic acid	5-40	4-32	0.55-4.4
Aldehydes (as CH_2O)	10-100	2-20	0.28-2.8
Carbon monoxide	1,000-10,000	180-1,800	24.8-248
Carbon dioxide	6,000-50,000	1,740-14,500	239-2,000
Sulfur dioxide	50-200	21-84	2.9-11.5
Naphthoquinone[b]	10-30	5.1-15	0.7-2.1

[a] For a production rate of 5.9×10^4 metric tons/yr.

[b] Only present when naphthalene is the feedstock.

Table 23. TYPICAL SCRUBBER VENT GAS COMPOSITION FOR *o*-XYLENE BASED PROCESS

Production rate = 5.9×10^{4} metric tons/yr
Temperature = 38°C
Gage pressure = 0 kPa

Component	Concentration, wt %	Average flow rate, kg/hr	Emission factor, g/kg
Phthalic anhydride	0.0017	3.2	0.44
Maleic anhydride	0.0044	8.2	1.13
Benzoic acid	0.0036	6.8	0.94
o-Tolualdehyde	-[a]	-[a]	-[a]
Phthalaldehyde	-[a]	-[a]	-[a]
Formaldehyde	-[a]	-[a]	-[a]
Acetaldehyde	-[a]	-[a]	-[a]
Acrolein	-[a]	-[a]	-[a]
Carbon monoxide	0.59	1,095.9	150.7
Carbon dioxide	2.03	3,784.6	520.4
Sulfur oxides	0.018	34.1	4.69
Nitrogen	75.62	140,897.3	19,373.
Oxygen	17.61	32,819.1	4,513.
Water	4.12	7,680.9	1,056.
Particulate	0.0025	4.6	0.63
Others	-[a]	-[a]	-[a]
Total	100.0	186,334.7	25,631

[a] Not reported in data source.

Table 24. TYPICAL SCRUBBER VENT GAS COMPOSITION FOR NAPHTHALENE BASED PROCESS

Production rate = 5.9 x 10^4 metric tons/yr
Temperature = 38°C
Gage pressure = 0 kPa

Component	Concentration, wt %	Average flow rate, kg/hr	Emission factor, g/kg
Phthalic anhydride	-[a]	3.0	0.41
Maleic anhydride	-[a]	1.0	0.14
Benzoic acid	-[a]	0.2	0.03
Naphthoquinone	-[a]	0.15	0.02
o-Tolualdehyde	-[a]	-[b]	-[b]
Phthalaldehyde	-[a]	-[b]	-[b]
Formaldehyde	-[a]	-[b]	-[b]
Acetaldehyde	-[a]	-[b]	-[b]
Acrolein	-[a]	-[b]	-[b]
Carbon monoxide	-[a]	366.	50.4
Carbon dioxide	-[a]	7,030.	967.
Sulfur oxides	-[a]	0.0	0.0
Nitrogen	-[a]	68,177.	9,378.
Oxygen	-[a]	12,208.	1,679.
Water	-[a]	-[b]	-[b]
Particulate	-[a]	4.6	0.63
Others	-[a]	-[b]	-[b]

[a] Not calculated because data lacking for one or more major components.

[b] Not reported in data source.

Table 25. TYPICAL INCINERATOR FLUE GAS COMPOSITION FOR o-XYLENE BASED PROCESS WITH SCRUBBER-INCINERATOR COMBINATION

Production rate = 5.9×10^4 metric tons/yr
Temperature = 927°C
Gage pressure = 0 kPa

Component	Concentration, wt %	Average flow rate, kg/hr	Emission factor, g/kg
Phthalic anhydride	-[a]	-[a]	-[a]
Maleic anhydride	-[a]	-[a]	-[a]
Benzoic acid	0.020	3.6	0.50
o-Tolualdehyde	-[a]	-[a]	-[a]
Phthalaldehyde	-[a]	-[a]	-[a]
Formaldehyde	-[a]	-[a]	-[a]
Acetaldehyde	-[a]	-[a]	-[a]
Acrolein	-[a]	-[a]	-[a]
Carbon monoxide	0.10	18.2	2.50
Carbon dioxide	15.47	2,759.	379.
Sulfur oxides	-[a]	-[a]	-[a]
Nitrogen oxides	0.0079	1.4	0.19
Nitrogen	54.17	9,661.	1,328.
Oxygen	2.22	395.4	54.4
Water	27.99	4,992.	686.
Methane	-[a]	-[a]	-[a]
Ethane	-[a]	-[a]	-[a]
Particulate	0.018	3.2	0.44
Others	-[a]	-[a]	-[a]
Total	100.0	17,834	2,451

[a] Not reported in data source.

Table 26. TYPICAL INCINERATOR FLUE GAS COMPOSITION FOR NAPHTHALENE BASED PROCESS WITH SCRUBBER-INCINERATOR COMBINATION

Production rate = 5.9 x 10^4 metric tons/yr

Temperature = 927°C

Gage pressure = 0 kPa

Component	Concentration, wt %	Average flow rate, kg/hr	Emission factor, g/kg
Phthalic anhydride	–[a]	1.75	0.24
Maleic anhydride	–[a]	0.87	0.12
Benzoic acid	–[a]	0.15	0.02
Naphthoquinone	–[a]	0.07	0.01
o-Tolualdehyde	–[a]	–[b]	–[b]
Phthalaldehyde	–[a]	–[b]	–[b]
Formaldehyde	–[a]	–[b]	–[b]
Acetaldehyde	–[a]	–[b]	–[b]
Acrolein	–[a]	–[b]	–[b]
Carbon monoxide	–[a]	18.2	2.50
Carbon dioxide	–[a]	–[b]	–[b]
Sulfur oxides	–[a]	–[b]	–[b]
Nitrogen oxides	–[a]	1.4	0.19
Nitrogen	–[a]	–[b]	–[b]
Oxygen	–[a]	–[b]	–[b]
Water	–[a]	–[b]	–[b]
Methane	–[a]	–[b]	–[b]
Ethane	–[a]	–[b]	–[b]
Particulate	–[a]	3.2	0.44
Others	–[a]	–[b]	–[b]

[a] Not calculated because data lacking for one or more major components.

[b] Not reported in data source.

employing direct incineration are presented in Tables 27[13] and 28.[26]

The composition of the incinerator flue gas depends upon incineration temperature, combustion efficiency, type of incinerator (thermal or catalytic), and feed material composition. Incinerator temperature determines the nitrogen oxides content of the stream due to oxygen fixation of nitrogen, while combustion efficiency governs the quantities of feed materials burned. Feed material composition determines the overall composition of the stack gas.

Removal efficiencies of up to 99% of organic materials are reported for a thermal incinerator in series with a water scrubber.[38] In the case of direct thermal incineration of the switch-condenser off-gas, efficiencies of 96.5% for organic material and 99.9% for carbon monoxide have been attained.[13] One difficulty with the latter method of control is that the entire contaminant load exhausts to the atmosphere during periods of incinerator flame-out, which occur an average of six times per year.[13] Nevertheless, the available data indicate that direct thermal incineration is the best overall method of control at the present time (see Section V.A).

3. Storage Tank Vents

The emissions from feedstock, crude product, and refined product storage tank vents (stream 34, 35, and 35 in Figure 2; streams 27, 28, and 29 in Figure 5) for a 5.9 x 10^4 metric tons/yr production rate have been estimated and are presented in Table 29. These estimates were obtained using the data in Tables 7 and 14 together with the empirical correlations

Table 27. TYPICAL INCINERATOR FLUE GAS COMPOSITION FOR o-XYLENE BASED PROCESS USING DIRECT THERMAL INCINERATION[13]

Production rate = 5.9 x 10^4 metric tons/yr
Temperature = 250°C
Gage pressure = 0 kPa

Component	Concentration, wt %	Average flow rate, kg/hr	Emission factor, g/kg
Phthalic anhydride	–[a]	4.0	0.55
Maleic anhydride	–[a]	13.2	1.82
Benzoic acid	–[a]	0.8	0.11
o-Tolualdehyde	–[a]	–[b]	–[b]
Phthalaldehyde	–[a]	–[b]	–[b]
Formaldehyde	–[a]	–[b]	–[b]
Acetaldehyde	–[a]	–[b]	–[b]
Acrolein	–[a]	–[b]	–[b]
Carbon monoxide	–[a]	0.9	0.125
Carbon dioxide	–[a]	–[b]	–[b]
Sulfur oxides	–[a]	36.4	5.0
Nitrogen oxides	–[a]	9.1	1.25
Nitrogen	–[a]	–[b]	–[b]
Oxygen	–[a]	–[b]	–[b]
Water	–[a]	–[b]	–[b]
Methane	–[a]	–[b]	–[b]
Ethane	–[a]	–[b]	–[b]
Particulate	–[a]	1.8	0.25
Others	–[a]	–[b]	–[b]

[a] Not calculated because data lacking for one or more major components.

[b] Not reported in data source.

Table 28. TYPICAL INCINERATOR FLUE GAS COMPOSITION FOR NAPHTHALENE BASED PROCESS USING DIRECT THERMAL INCINERATION[26]

Production rate = 5.9 x 10^4 metric tons/yr
Temperature = 250°C
Gage pressure = 0 kPa

Component	Concentration, wt %	Average flow rate, kg/hr	Emission factor, g/kg
Phthalic anhydride	–[a]	5.2	0.71
Maleic anhydride	–[a]	1.8	0.24
Benzoic acid	–[a]	0.4	0.05
Naphthoquinone	–[a]	0.15	0.02
o-Tolualdehyde	–[a]	–[b]	–[b]
Phthalaldehyde	–[a]	–[b]	–[b]
Formaldehyde	–[a]	–[b]	–[b]
Acetaldehyde	–[a]	–[b]	–[b]
Acrolein	–[a]	–[b]	–[b]
Carbon monoxide	–[a]	0.4	0.05
Carbon dioxide	–[a]	–[b]	–[b]
Sulfur oxides	–[a]	–[b]	–[b]
Nitrogen oxides	–[a]	9.1	1.25
Nitrogen	–[a]	–[b]	–[b]
Oxygen	–[a]	–[b]	–[b]
Water	–[a]	–[b]	–[b]
Methane	–[a]	–[b]	–[b]
Ethane	–[a]	–[b]	–[b]
Particulate	–[a]	1.8	0.25
Others	–[a]	–[b]	–[b]

---

[a] Not calculated because data lacking for one or more major components.

[b] Not reported in data source.

Table 27. TYPICAL INCINERATOR FLUE GAS COMPOSITION FOR *o*-XYLENE BASED PROCESS USING DIRECT THERMAL INCINERATION[13]

Production rate = 5.9×10^4 metric tons/yr
Temperature = 250°C
Gage pressure = 0 kPa

Component	Concentration, wt %	Average flow rate, kg/hr	Emission factor, g/kg
Phthalic anhydride	–[a]	4.0	0.55
Maleic anhydride	–[a]	13.2	1.82
Benzoic acid	–[a]	0.8	0.11
o-Tolualdehyde	–[a]	–[b]	–[b]
Phthalaldehyde	–[a]	–[b]	–[b]
Formaldehyde	–[a]	–[b]	–[b]
Acetaldehyde	–[a]	–[b]	–[b]
Acrolein	–[a]	–[b]	–[b]
Carbon monoxide	–[a]	0.9	0.125
Carbon dioxide	–[a]	–[b]	–[b]
Sulfur oxides	–[a]	36.4	5.0
Nitrogen oxides	–[a]	9.1	1.25
Nitrogen	–[a]	–[b]	–[b]
Oxygen	–[a]	–[b]	–[b]
Water	–[a]	–[b]	–[b]
Methane	–[a]	–[b]	–[b]
Ethane	–[a]	–[b]	–[b]
Particulate	–[a]	1.8	0.25
Others	–[a]	–[b]	–[b]

[a] Not calculated because data lacking for one or more major components.

[b] Not reported in data source.

Table 28. TYPICAL INCINERATOR FLUE GAS COMPOSITION FOR NAPHTHALENE BASED PROCESS USING DIRECT THERMAL INCINERATION[26]

Production rate = 5.9 x 10^4 metric tons/yr

Temperature = 250°C

Gage pressure = 0 kPa

Component	Concentration, wt %	Average flow rate, kg/hr	Emission factor, g/kg
Phthalic anhydride	–[a]	5.2	0.71
Maleic anhydride	–[a]	1.8	0.24
Benzoic acid	–[a]	0.4	0.05
Naphthoquinone	–[a]	0.15	0.02
o-Tolualdehyde	–[a]	–[b]	–[b]
Phthalaldehyde	–[a]	–[b]	–[b]
Formaldehyde	–[a]	–[b]	–[b]
Acetaldehyde	–[a]	–[b]	–[b]
Acrolein	–[a]	–[b]	–[b]
Carbon monoxide	–[a]	0.4	0.05
Carbon dioxide	–[a]	–[b]	–[b]
Sulfur oxides	–[a]	–[b]	–[b]
Nitrogen oxides	–[a]	9.1	1.25
Nitrogen	–[a]	–[b]	–[b]
Oxygen	–[a]	–[b]	–[b]
Water	–[a]	–[b]	–[b]
Methane	–[a]	–[b]	–[b]
Ethane	–[a]	–[b]	–[b]
Particulate	–[a]	1.8	0.25
Others	–[a]	–[b]	–[b]

[a] Not calculated because data lacking for one or more major components.

[b] Not reported in data source.

Table 29. STORAGE TANK WORKING AND BREATHING LOSSES FOR A 5.9 x 10^4 METRIC TONS/YR PHTHALIC ANHYDRIDE PLANT

Process raw material	Species	Uncontrolled emission rate, kg/hr	Uncontrolled emission factor, g/kg	Controlled emission rate, kg/hr	Controlled emission factor, g/kg	Control efficiency, %
o-Xylene	o-Xylene	1.38	0.19	0.014	0.002	99
	Phthalic anhydride (crude)	0.80	0.11	0.008	0.001	99
	Phthalic anhydride (refined)	2.04	0.28	0.020	0.003	99
Naphthalene	Naphthalene	4.36	0.60	0.044	0.006	99
	Phthalic anhydride (crude)	1.16	0.16	0.012	0.002	99
	Phthalic anhydride (refined)	1.40	0.19	0.014	0.002	99

for petrochemical losses from storage tanks which have been formulated by the American Petroleum Institute.[39-43] The correlations give uncontrolled emission rates; the controlled emission rates listed in Table 29 are based on a control efficiency of 99%.[44] The estimated accuracy of the empirical correlations is ±10%.[39-43] Calculations are presented in the Appendix.

Emission control devices presently in use comprise conservation vents on o-xylene and naphthalene tanks, and condensers or sublimation boxes on crude and refined phthalic anhydride tanks. Phthalic anhydride tanks may, alternatively, be vented to the incinerator for control. However, it is common practice to vent some or all of the storage tanks directly to the atmosphere.

4. Flaker and Bagger Vent

The vent from the flaking and bagging operations (stream 33 in Figure 2; stream 26 in Figure 5) is a continuous source

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[39] Evaporation Loss from Fixed Roof Tanks. American Petroleum Institute. New York. API Bulletin No. 2518. 1962. 38 p.

[40] Use of Variable Vapor Space Systems to Reduce Evaporation Loss. American Petroleum Institute. New York. API Bulletin No. 2520. 1964. 14 p.

[41] Petrochemical Evaporation Loss from Storage Tanks. American Petroleum Insittute. New York. API Bulletin No. 2523. 1969. 14 p.

[42] Evaporation Loss from Floating Roof Tanks. American Petroleum Institute. New York. API Bulletin No. 2517. 1962. 13 p.

[43] Evaporation Loss in the Petroleum Industry - Causes and Control. American Petroleum Institute. New York. API Bulletin No. 2513. 1959. 57 p.

[44] Personal communication, R. G. Lunche and A. B. Netzley, Los Angeles County Air Pollution Control District. March 28, 1975.

of particulate emissions. This stream, which contains phthalic anhydride as the only contaminant, is ducted to a cyclone separator or baghouse for recovery of the solid product. For a 5.9 x 10^4 metric tons/yr plant, the uncontrolled emission rate for this stream is estimated to be 0.7 kg/hr of phthalic anhydride, with a corresponding emission factor of 0.1 g/kg.[26] The controlled emission rate is 0.007 kg/hr, with a corresponding emission factor of 0.001 g/kg, assuming that a control efficiency of 99% is achieved with a bag filter.[44]

5. Transport Loading Facility Vent

The liquid product transport loading facility vent (stream 37 in Figure 2; stream 31 in Figure 5) is a continuous source of atmospheric emissions. The only contaminant in this stream is phthalic anhydride. Using the emission factor data listed in Reference 45, the uncontrolled emission rate for this stream is estimated to be 3.3 kg/hr of phthalic anhydride, based on an emission factor of 0.45 g/kg loaded, a production rate of 5.9 x 10^4 metric tons/yr, and 100% of product shipped in liquid form. A control efficiency of 99% was assumed, based on the data in Reference 45. This yields a controlled emission rate of 0.03 kg/hr and a controlled emission factor of 0.005 g/kg phthalic anhydride produced. The accuracy of these values is considered to be equivalent to that for storage tanks, i.e., ±10% for uncontrolled emissions.[46]

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[45] Air Pollution Engineering Manual, 2nd Edition. Danielson, J. A. (ed.). Environmental Protection Agency. Research Triangle Park. Publication No. AP-40. May 1973. 987 p.

[46] Personal communication. W. Fitzgibbons, Standard Oil of Ohio (SOHIO). June 23, 1975.

6. Catalyst Storage Hopper Vents

The vents on the storage facilities for active and spent catalyst are intermittent sources of emissions from naphthalene based plants. The emissions consist of the fines fraction (primarily particles <40 μm in diameter) of the vanadium oxide catalyst, which is described in Table 15. Both vanadium oxide and silica dusts are respiratory irritants, and vanadium oxide can be toxic if taken internally.[34] Emissions occur during catalyst transfer operations in which the catalyst is conveyed pneumatically from the reactor system to the storage hoppers. Cyclone separators are employed on the hopper vents to recover the entrained catalyst particles from the air stream.

The uncontrolled emission rate from the spent catalyst storage vent in a 4.08×10^4 metric tons/yr plant is 295 kg/hr.[37] The operation is intermittent with a total duration of approximately 50 hr/yr. The uncontrolled emission factor is therefore 0 36 g/kg. The controlled emission rate is 4.6 kg/hr, and the corresponding emission factor is approximately 0.005 g/kg. Thus, the control efficiency is 98.5%.

The uncontrolled emission rate from the active catalyst storage vent in a 4.08×10^4 metric tons/yr plant is 22.7 kg/hr.[37] The emissions occur an average of four to eight times per year and have a duration of approximately 12 hours per occurrence. Thus, the uncontrolled emission factor is approximately 0.05 g/kg. The controlled emission rate is 2.3 kg/hr, and the corresponding emission factor is 0.005 g/kg. The control efficiency is therefore 90%.

The uncontrolled and controlled emission factors for the combined catalyst storage vents are 0.41 g/kg and 0.01 g/kg, respectively, resulting in a combined control efficiency of 97.5%.

7. Fugitive Emissions

Fugitive emissions from phthalic anhydride manufacture originate from a number of sources: pump seals, flanges, valves, and compressor seals. In addition to these losses that occur under normal operating conditions, operating upsets can result in emissions of fluid from the heat-transfer circuits associated with the switch condensers and the product purification section of the plant. A typical heat-transfer fluid used in phthalic anhydride plants is Dowtherm A, a eutectic mixture of diphenyl oxide (73.5%) and diphenyl (26.5%). This material has a very noticeable odor which has been described as that of rose-geranium.[14] Diphenyl oxide has an odor threshold of between 0.01 ppm and 0.001 ppm by volume.[14]

The most frequently used organic heat-transfer fluids are listed in Table 30 together with their compositions and usable temperature ranges.[16,17] Also listed are the threshold limit values (TLV's).[47] Of the fluids listed, Mobiltherm Light® and Therminol 66® are known to be used in phthalic anhydride plants.[13] Emissions of these fluids are in the form of aerosol mists, which reportedly settle in the immediate vicinity of the source.[13] It is estimated that 95% of these emissions originate from the switch-condenser heat-transfer circuit.[13]

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[47] Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1975. American Conference of Governmental Industrial Hygienists. Cincinnati. 1975. 97 p.

Table 30. FREQUENTLY USED HEAT-TRANSFER FLUIDS[a]

Name	Composition	Usable temperature range, °C	TLV, g/m^3
Dowtherm A[b]	Diphenyl-diphenyl oxide eutectic	16 to 400	0.001
Dowtherm E	o-Dichlorobenzene	-18 to 260	0.300
Dowtherm G	Di- and tri-aryl ethers	-10 to 345	
Dowtherm H	Aromatic oil	-10 to 290	
Dowtherm J	Alkylated aromatic	-75 to 300	
Humbletherm 500	Aliphatic oil	-20 to 315	
Mobiltherm Light	Aromatic oil	-30 to 205	
Mobiltherm 600	Alkylated aromatic	-20 to 315	
Mobiltherm 603	Paraffinic oil	-18 to 315	
Therminol 44	Modified ester	-50 to 220	
Therminol 55	Alkylated aromatic	-18 to 315	
Therminol 60	Aromatic hydrocarbon	-50 to 315	
Therminol 66	Modified terphenyl	-7 to 345	0.009
Therminol 77	Polyphenyl ether	16 to 370	0.007
Therminol 88	Mixed terphenyl	145 to 425	0.009
Therminol FR-1	Polychlorinated biphenyl	-4 to 315	0.005
Ucon 50-HB-280X	Ether of polyalkylene oxide	-18 to 260	

[a] Composition and usable temperature data for most of the heat-transfer fluids are reprinted with permission from Chemical Engineering, May 28, 1973, Copyright (c), McGraw-Hill, Inc., New York, N.Y. 10020

[b] Other trade names include Thermex, Therm-S, Diphyl, and Therminol VP-1.

In the Badger-Sherwin-Williams process, product purification is a batch operation. Hence, fugitive emissions can arise from the batch filling and dumping of process vessels. In addition, emissions of vanadium oxide catalyst dust may occur during catalyst loading and unloading operations. Estimates of fugitive emissions are summarized in Table 31.[13,26] It has been assumed that the heat-transfer fluid is Dowtherm A, which is listed as diphenyl oxide, its major component.

Table 31. FUGITIVE EMISSIONS FROM PHTHALIC ANHYDRIDE PLANTS

Compound	Average emission rate, kg/hr[a]	Emission factor, g/kg
Phthalic anhydride		
Maleic anhydride		
Benzoic acid		
Naphthoquinone[b]		
Diphenyl oxide	0.12	0.016
Vanadium oxide catalyst[b]		
o-Xylene[c]		
Naphthalene[b]		
Formaldehyde		
Acetaldehyde		
Phthalaldehyde		
o-Tolualdehyde		
Acrolein		
Dihydroxynaphthalene[b]		
Combined hydrocarbons[d]	0.73	0.10

[a] For a 5.9 x 10^4 metric tons/yr plant.

[b] Naphthalene based plants only.

[c] o-Xylene based plants only.

[d] Does not include diphenyl oxide.

Note: Blanks indicate data not available.

8. Dual Thermal Incineration

Available data[13,26] indicate that the best presently feasible method of control utilizes direct thermal incineration of the switch-condenser off-gas together with a secondary thermal incinerator to treat the waste streams from the product purification section of the plant (see Section V.A). Typical compositions and emission rates for the latter unit are presented in Table 32 for an o-xylene based plant.[13] This unit treats

Table 32. TYPICAL FLUE GAS COMPOSITION FOR DUAL INCINERATOR

Production rate = 5.9×10^4 metric tons/yr
Temperature = 760°C
Gage pressure = 0 kPa

Component	Concentration, wt %	Average flow rate, kg/hr	Emission factor, g/kg
Phthalic anhydride	0.010	0.8	0.11
Maleic anhydride	0.0037	0.3	0.04
Benzoic acid	0.0012	0.1	0.0125
o-Tolualdehyde			
Phthalaldehyde			
Formaldehyde			
Acetaldehyde			
Acrolein			
Carbon monoxide	0.11	9.1	1.25
Carbon dioxide	5.55	455.	62.6
Sulfur oxides			
Nitrogen oxides	0.011	0.9	0.125
Nitrogen	55.47	4,545.	625.
Oxygen	8.32	682.	93.8
Water	30.51	2,500.	344.
Methane			
Ethane			
Particulate	0.011	0.9	0.125
Others			
Total	100.0	8,194.	1,127.

Note: Blanks indicate data not reported.

all of the waste streams from the product purification section of the plant, and reportedly achieves a control efficiency of 99% for combined organics. The applicability of such a unit to naphthalene based plants is uncertain since product purification is a batch operation in these plants. However, no fundamental barrier to its use in naphthalene based plants is apparent.

C. ENVIRONMENTAL EFFECTS

1. Definition of a Representative Source

For the purpose of assessing the source severity, a representative o-xylene based phthalic anhydride plant is defined to be one using the BASF process and having a production capacity of 5.9×10^4 metric tons/yr. The BASF process is specified because it is the newest and most widely used technology, accounting for 79% of the o-xylene based production in 1974.[3,4] The standard size BASF plant has two production trains of two reactors each, and has a capacity of 5.9×10^4 metric tons/yr. The seven o-xylene based plants operating in the United States range in capacity from 1.59×10^4 to 7.94×10^4 metric tons/yr with a mean value of 4.28×10^4 metric tons/yr.

A representative naphthalane based phthalic anhydride plant is defined to be one using the Badger-Sherwin-Williams process and having a production capacity of 5.9×10^4 metric tons/yr. The Badger-Sherwin-Williams process is the dominant fluid-bed technology and accounted for 73% of the naphthalene based production in 1974.[3,4] There is no standard size for the Badger-Sherwin-Williams fluid-bed reactors. Hence, the representative source capacity was chosen so as to place the source severity calculations on the same basis as that used for o-xylene based production. The three naphthalene based plants range in size from 4.08 x 10^4 to 6.8 x 10^4 metric tons/yr with a mean production capacity of 4.99 x 10^4 metric tons/yr.

The source severity is assessed on the basis that the best available control technology is applied to the representative source. This implies that the switch-condenser off-gas is controlled by direct thermal incineration and that a secondary thermal incinerator is employed to treat all of the waste streams from the product purification section of the plant. (See Section V.A.) The dual thermal incineration system is currently used in two of the four plants employing the BASF process, and will probably be installed in other plants in the future. It is also assumed that all storage tank vents, as well as the transport loading facility vent, are fully controlled. In addition, the flaker and bagger vent is assumed to be equpped with a suitable bag filter.

2. Emission Factors

Emission factors for an o-xylene based plant equipped with a dual incineration control systemare given in Table 33. The data were obtained from References 13 and 26, except as noted. The control efficiencies of the two incinerators were measured only for total organic material. In order to obtain controlled emission factors of individual organic species it was assumed that they were controlled with this same efficiency. Error bounds on the emission factors were estimated wherever possible. The bounds on uncontrolled emission factors for the two incinerators were taken directly from Reference 13. Those for storage tanks and transport loading were obtained from References 39-43, and Reference 46, respectively. The bounds on controlled emission factors were taken to be somewhat higher in order to reflect the uncertainty in the control efficiencies of individual species. The threshold limit values (TLV's of the individual species, as given in Reference 47, are also listed in Table 33.

Table 33. EMISSION FACTORS FOR *o*-XYLENE BASED PHTHALIC ANHYDRIDE PLANTS[3,26]

Species	TLV, g/m³	Emission factor, g/kg		Control efficiency, %
		Uncontrolled	Controlled	
Particulate	0.010			
Main process incinerator		–[a]	0.25 ± 50%	-
Secondary incinerator		–[a]	0.125 ± 50%	-
Flaker and bagger		0.10	0.001	99[b]
Sulfur oxides	0.013			
Main process incinerator		5.0 ± 25%	5.0 ± 25%	0
Nitrogen oxides	0.009			
Main process incinerator		–[c]	1.25 ± 50%	-
Secondary incinerator		–[c]	0.125 ± 25%	-
Carbon monoxide	0.055			
Main process incinerator		125.0 ± 20%	0.125 ± 50%	99.9
Secondary incinerator		–[c]	1.25 ± 50%	-
Maleic anhydride	0.001			
Main process incinerator		52.0 ± 20%	1.82 ± 25%	96.5[d]
Secondary incinerator		3.75 ± 83%	0.038 ± 90%	99[d]
Phthalic anhydride	0.006			
Main process incinerator		15.6 ± 20%	0.545 ± 25%	96.5[d]
Secondary incinerator		10.6 ± 53%	0.106 ± 60%	99[d]
Storage tanks		0.28 ± 10%[e,f]	0.003 ± 20%	99[b]
Flaker and bagger		0.10	0.001	99[b]
Transport loading		0.45 ± 10%[g]	0.005 ± 20%[g]	99[g]
Fugitive emissions		–[a]	–[h]	-
Benzoic acid	0.050			
Main process incinerator		3.12 ± 20%	0.109 ± 25%	96.5[d]
Secondary incinerator		1.25 ± 50%	0.0125 ± 55%	99[d]
Diphenyl oxide	0.001			
Fugitive emissions		0.016	–[h]	-
o-Xylene	0.435			
Storage tanks		0.19 ± 10%[e]	0.002 ± 20%	99[b]
Formaldehyde	0.003			
Main process incinerator		2.1[b,i]	0.074[i]	96.5[d]
Secondary incinerator		–[a]	–[a]	-
Acetaldehyde	0.180			
Main process incinerator		–[a]	–[a]	-
Secondary incinerator		–[a]	–[a]	-
Phthalaldehyde	–[j]			
Main process incinerator		–[a]	–[a]	-
Secondary incinerator		–[a]	–[a]	-
o-Tolualdehyde	–[j]			
Main process incinerator		–[a]	–[a]	-
Secondary incinerator		–[a]	–[a]	-
Acrolein	0.00025			
Main process incinerator		–[a]	–[a]	-
Secondary incinerator		–[a]	–[a]	-
Total hydrocarbons[k]	0.067			
Main process incinerator		72.8 ± 30%[l]	2.6 ± 30%	96.5
Secondary incinerator		18.8 ± 60%	0.16 ± 60%	99
Storage tanks		0.47 ± 10%	0.005 ± 20%	99[b]
Flaker and bagger		0.1	0.001	99[b]
Transport loading		0.45[g]	0.005[g]	99[g]
Fugitive emissions		0.116	–[h]	-

[a] Data not available.

[b] Estimate based on data from Reference 44.

[c] No emissions generated in uncontrolled process.

[d] Assumed equal to value measured for total organics in Reference 13.

[e] Calculated using empirical correlations given in References 39-43.

[f] Value is for refined product storage only; crude product storage tanks are vented to the main process incinerator.

[g] Value for loading racks given in Reference 45.

[h] Fugitive emissions are not controlled.

[i] Total aldehydes reported as formaldehyde in Reference 44.

[j] TLV not defined.

[k] Includes all non-methane organic species.

[l] Includes 3.2 g/kg unspecified organic residues.

Emission factors for a naphthalene based plant equipped with a dual incineration control system are presented in Table 34. The data were obtained from Reference 26, except as noted. It was assumed that this control system could be applied to a naphthalene based plant without having its control efficiency altered. It was also assumed that the particulate and nitrogen oxides emissions from the two incinerators would be the same as the corresponding values for an o-xylene based plant. Error bounds for emission factors from the two incinerators were assigned on the basis of (1) the corresponding values for an o-xylene based plant; (2) the fact that the accuracy of the data for naphthalene based production is believed to be generally poorer than that for o-xylene based production; and (3) the ranges for uncontrolled emission factors given in Table 22. Error bounds on emission factors for storage tanks and transport loading are the same as those for o-xylene based production.

3. Source Severity

In order to obtain a quantitative measure of the hazard potential of phthalic anhydride production, the source severity, S, is defined as:

$$S = \frac{\bar{\chi}_{max}}{F} \qquad (1)$$

where $\bar{\chi}_{max}$ is the maximum time-averaged ground level concentration of each pollutant emitted from a representative plant, and F is defined as a primary ambient air quality standard for criteria pollutants (particulate, SO_x, NO_x, CO and hydrocarbons), while for non-criteria pollutants,

$$F \equiv TLV \cdot 8/24 \cdot 0.01,\ g/m^3$$

The factor 8/24 adjusts the TLV for continuous rather than workday exposure, and the factor of 0.01 accounts for the fact that the general population is a higher risk group than healthy workers.

Table 34. EMISSION FACTORS FOR NAPHTHALENE BASED PHTHALIC ANHYDRIDE PLANTS[26]

Species	TLV, g/m^3	Emission factor, g/kg		Control efficiency, %
		Uncontrolled	Controlled	
Particulate	0.010			
Main process incinerator		-[a]	0.25 ± 70%	-
Secondary incinerator		-[a]	0.125 ± 70%	-
Flaker and bagger		0.10	0.001	99[b]
Nitrogen oxides	0.009			
Main process incinerator		-[c]	1.25 ± 70%	-
Secondary incinerator		-[c]	0.125 ± 40%	-
Carbon monoxide	0.055			
Main process incinerator		50.5 ± 50%	0.05 ± 70%	99.9
Secondary incinerator		-	1.25 ± 70%	-
Phthalic anhydride	0.006			
Main process incinerator		20.4 ± 40%	0.71 ± 50%	96.5[d]
Secondary incinerator		9.8 ± 70%	0.10 ± 80%	99[d]
Storage tanks		0.35 ± 10%[e,f]	0.0004 ± 20%	99[b]
Flaker and bagger		0.10	0.001	99[b]
Transport loading		0.45 ± 10%[g]	0.005 ± 20%[g]	99[g]
Fugitive emissions		-[a]	-[h]	-
Maleic acid	0.001			
Main process incinerator		7.0 + 200%[i]	0.24 + 200%[i]	96.5[d]
Secondary incinerator		4.9 ± 80%	0.05 ± 90%	99[d]
Benzoic acid	0.050[j]			
Main process incinerator		1.56 ± 40%	0.05 ± 50%	96.5[d]
Secondary incinerator		-[a]	-[a]	-
Naphthoquinone	0.0004[k]			
Main process incinerator		0.69 ± 40%	0.02 ± 50%	96.5[d]
Secondary incinerator		6.6 ± 70%	0.07 ± 80%	99[d]
Naphthalene	0.050			
Storage tanks		0.60 ± 10%[e]	0.006 ± 20%	99[b]

[a] Data not available.

[b] Estimate based on data from Reference 44.

[c] No emissions generated in uncontrolled process.

[d] Assumed equal to value measured for total organics in Reference 13.

[e] Calculated using empirical correlations given in References 39-43.

[f] Includes both refined and crude product storage tanks.

[g] Value for loading racks given in Reference 45.

[h] Fugitive emissions are not controlled.

[i] Uncontrolled emission factor of 7.0 g/kg, obtained from Reference 26, is believed to be low; compare Table 22.

[j] Estimate based on the value of 0.080 for benzene.

[k] TLV for naphthoquinone assumed equal to the value for quinone.

Table 34 (continued). EMISSION FACTORS FOR NAPHTHALENE BASED PHTHALIC ANHYDRIDE PLANT[26]

Species	TLV, g/m^3	Emission factor, g/kg		Control efficiency, %
		Uncontrolled	Controlled	
Vanadium oxide catalyst	0.00056[l]			
Catalyst storage		0.41	0.01	97.5
Fugitive emissions		-[a]	-[a]	-
Diphenyl oxide	0.001			
Fugitive emissions		0.016	-[h]	
Formaldehyde	0.003			
Main process incinerator		2.1[b,m]	0.074[m]	96.5[d]
Secondary incinerator		-[a]	-[a]	-
Acetaldehyde	0.180			
Main process incinerator		-[a]	-[a]	-
Secondary incinerator		-[a]	-[a]	-
Phthalaldehyde	-[h]			
Main process incinerator		-[a]	-[a]	-
Secondary incinerator		-[a]	-[a]	-
o-Tolualdehyde	-[n]			
Main process incinerator		-[a]	-[a]	-
Secondary incinerator		-[a]	-[a]	-
Acrolein	0.00025			
Main process incinerator		-[a]	-[a]	-
Secondary incinerator		-[a]	-[a]	-
Dihydroxynaphthalene	-[n]			
Main process incinerator		-[a]	-[a]	-
Secondary incinerator		-[a]	-[a]	-
Total hydrocarbons[o]	0.067			
Main process incinerator		3.18 + 79% − 35%	1.09 + 85% − 40%	96.5
Secondary incinerator		26.5 ± 70%[p]	0.27 ± 80%	99
Storage tanks		0.95 ± 10%	0.01 ± 20%	99[b]
Flaker and bagger		0.1	0.001	99[b]
Transport loading		0.45[g]	0.005[g]	99[g]
Fugitive emissions		0.116	-[h]	-

[a] Data not available.

[b] Estimate based on data from Reference 44.

[d] Assumed equal to value measured for total organics in Reference 13.

[h] Fugitive emissions are not controlled.

[l] Calculated using the rule for mixtures given in Reference 47, the catalyst composition given in Table 15, and the following individual TLV's: V_2O_5, 0.00089 g/m^3; SiO_2, 0.0003 g/m^3 for total dust, respirable and nonrespirable; SO_3, 0.013 g/m^3. The TLV for V_2O_5 was obtained by multiplying the listed value of 0.0005 g/m^3 V_2O_5 as V by the factor (182 g V_2O_5)/(102 g V) = 1.78 In lieu of other information, the TLV of K_2SO_4 was assumed to be large compared with those of the other components. Thus,

$$\text{TLV}_{\text{catalyst}} \equiv \frac{1}{\frac{0.09}{0.00089} + \frac{0.5}{0.0003} + \frac{0.12}{0.013}} = 0.00056\ g/m^3$$

[m] Total aldehydes reported as formaldehyde in Reference 44.

[n] TLV not defined.

[o] Includes all organic species.

[p] Includes 5.2 g/kg unspecified organic residues.

Thus, the source severity represents the ratio of the maximum mean ground level exposure to the hazard level of exposure for a given pollutant.

The maximum ground level concentration, χ_{max}, is calculated according to Gaussian plume dispersion theory:

$$\chi_{max} = \frac{2Q}{\pi H^2 e \bar{u}} \tag{2}$$

where Q = mass emission rate, g/sec
$\bar{u}$ = average wind speed, m/sec
H = effective emission height, m
e = 2.72

Equation (2) yields a value for a short-term averaging time during which the Gaussian plume dispersion equation is valid. The short-term averaging time was found to be 3 minutes in a study of published data on lateral and vertical diffusion.[48] For a continuously emitting source, the maximum mean ground level concentration for time intervals between 3 minutes and 24 hours can be estimated from the relation:[49]

$$\bar{\chi}_{max} = \chi_{max} \left(\frac{t_0}{t}\right)^{0.17} \tag{3}$$

where t = the averaging time
t_0 = the short-term averaging time (3 min.)

For non-criteria pollutants, the averaging time, t, is 24 hours. For criteria pollutants, the averaging times are those used in the definition of the primary ambient air quality standards. The only exception is NO_x, for which the primary standard averaging time is one year. Since Equation (3) is not valid for averaging times of this magnitude, the calculation of $\overline{\chi}_{max}$ for NO_x is based on Equation (5.13) of Reference 49, which estimates the annual average ground level concentration.

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[48] Nonhebel, G. Recommendations on Heights for New Industrial Chimneys. Journal of the Institute of Fuel. 33:479-511, July 1960.

[49] Turner, D. B. Workbook of Atmospheric Dispersion Estimates. U.S. Department of Health, Education, and Welfare, Public Health Service. Cincinnati. Publication No. 999-AP-26. 1969. 64 p.

Insertion of the national average wind speed of 4.5 m/sec into the above equations leads to the severity factor equations listed in Table 35. The emission heights which were used in the calculations are given in Table 36. The heights for the two incinerators were obtained from Reference 13, that for the flaker and bagger from Reference 50, and the others were estimated. The emission rates, Q, were obtained from the controlled emission factors in Tables 33 and 34. The resulting severity factors are tabulated in Tables 37 and 38 for o-xylene and naphthalene based plants, respectively. In these calculations, it was assumed that Gaussian plume dispersion theory is equally valid for all emissions, irrespective of their chemical, physical, or topological characteristics.

The largest value of the severity factor in Tables 37 and 38 is 18.5 for diphenyl oxide. This value is based on the assumption that Dowtherm A heat-transfer fluid is used in the plant. However, it is clear from the TLV's listed in Table 30 that the severity factor for this emission is highly dependent on the particular fluid used. Thus, assuming the same emission rate, the severity factor would be 37.0 for Therminol FR-1® and 0.06 for Dowtherm E.

The above severity factors for diphenyl oxide emissions and vanadium oxide catalyst emissions from catalyst storage

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[50] Personal communication, L. B. Evans, U.S. Environmental Protection Agency (Data originally supplied by Stepan Chemical Company). June 12, 1975.

Table 35. SOURCE SEVERITY EQUATIONS

Pollutant	S (dimensionless)
Particulate	$70\ QH^{-2}$
SO_x	$50\ QH^{-2}$
NO_x	$315\ QH^{-2.1}$
Hydrocarbons	$162.5\ QH^{-2}$
CO	$0.78\ QH^{-2}$
All others	$5.5\ QH^{-2}\ (TLV)^{-1}$

Q = emission rate, g/sec
H = emission height, m
TLV = threshold limit value, g/m^3

Table 36. EMISSION HEIGHTS FOR REPRESENTATIVE SOURCE

Source of emissions	Emission height, m
Main process incinerator	61.0
Secondary incinerator	30.5
Storage tanks	15.2
Flaker and bagger	6.1
Transport loading	6.1
Fugitive emissions	3.1
Catalyst storage	12.2

facilities were calculated by treating these intermittent sources as continuous sources with their respective annual emission rates. Severities calculated with emission rates based on the average duration of these emissions would be considerably higher. For instance, S = 216 for vanadium oxide catalyst emissions. Although the duration of the diphenyl oxide emissions is not known, the severity calculated on this basis would be correspondingly higher.

Table 37. SOURCE SEVERITY FACTORS FOR A REPRESENTATIVE o-XYLENE BASED PHTHALIC ANHYDRIDE PLANT

Compound	Source severity					
	Main process incinerator	Secondary incinerator	Storage tanks	Flaker and bagger	Transport loading	Fugitive emissions
Particulate	0.0095	0.019	–[a]	0.0038	–[a]	–[a]
Sulfur oxides	0.14	–[a]	–[a]	–[a]	–[a]	–[a]
Nitrogen oxides	0.14	0.061	–[a]	–[a]	–[a]	–[a]
Carbon monoxide	0.000053	0.0021	–[a]	–[a]	–[a]	–[a]
Total hydrocarbons[b]	0.23	0.056	0.0071	0.0088	0.044	4.0
Phthalic anhydride	0.28	0.20	0.024	0.050	0.24	–[c]
Maleic anhydride	5.4	0.45	–[a]	–[a]	–[a]	–[c]
Benzoic acid	0.0065	0.0030	–[a]	–[a]	–[a]	–[c]
Diphenyl oxide	–[a]	–[a]	–[a]	–[a]	–[a]	18.5
o-Xylene	–[a]	–[a]	0.00022	–[a]	–[a]	–[c]
Formaldehyde	0.074[d]	–[c]	–[a]	–[a]	–[a]	–[c]
Acetaldehyde	–[c]	–[c]	–[a]	–[a]	–[a]	–[c]
Phthaldehyde	–[c]	–[c]	–[a]	–[a]	–[a]	–[c]
o-Tolualdehyde	–[c]	–[c]	–[a]	–[a]	–[a]	–[c]
Acrolein	–[c]	–[c]	–[a]	–[a]	–[a]	–[c]

[a] No emissions.

[b] Includes all non-methane organic species.

[c] Data not available.

[d] Total aldehydes reported as formaldehyde.

Table 38. SOURCE SEVERITY FACTORS FOR A REPRESENTATIVE NAPHTHALENE BASED PHTHALIC ANHYDRIDE PLANT

Compound	Source Severity						
	Main process incinerator	Secondary incinerator	Storage tanks	Flaker and bagger	Transport loading	Catalyst storage	Fugitive emissions
Particulate	0.0095	0.019	-[a]	0.0038	-[a]	-[a]	-[a]
Nitrogen oxides	0.14	0.061	-[a]	-[a]	-[a]	-[a]	-[a]
Carbon monoxide	0.000021	0.0021	-[a]	-[a]	-[a]	-[a]	-[a]
Total hydrocarbons[b]	0.10	0.095	0.014	0.0088	0.044	-[a]	4.0
Phthalic anhydride	0.36	0.20	0.032	0.050	0.24	-[a]	-[c]
Maleic anhydride	0.72	0.60	-[a]	-[a]	-[a]	-[a]	-[c]
Benzoic acid	0.0030	-[a]	-[a]	-[a]	-[a]	-[a]	-[c]
Naphthoquinone	0.15	2.1	-[a]	-[a]	-[a]	-[a]	-[c]
Diphenyl oxide	-[a]	-[a]	-[a]	-[a]	-[a]	-[a]	18.5
Vanadium oxide catalyst	-[a]	-[a]	-[a]	-[a]	-[a]	1.4	-[c]
Naphthalene	-[a]	-[a]	0.0058	-[a]	-[a]	-[a]	-[c]
Formaldehyde	0.074[d]	-[c]	-[a]	-[a]	-[a]	-[a]	-[c]
Acetaldehyde	-[c]	-[c]	-[a]	-[a]	-[a]	-[a]	-[c]
Phthalaldehyde	-[c]	-[c]	-[a]	-[a]	-[a]	-[a]	-[c]
o-Tolualdehyde	-[c]	-[c]	-[a]	-[a]	-[a]	-[a]	-[c]
Acrolein	-[c]	-[c]	-[a]	-[a]	-[a]	-[a]	-[c]
Dihydroxynaphthalene	-[c]	-[c]	-[a]	-[a]	-[a]	-[a]	-[c]

[a] No emissions.

[b] Includes all non-methane organic species.

[c] Data not available

[d] Total aldehydes reported as formaldehyde.

4. Industry Contribution to Total Atmospheric Emissions

The mass emissions of criteria pollutants (particulate, SO_x, NO_x, CO, and hydrocarbons) resulting from phthalic anhydride production were calculated using the controlled emission factors from Tables 33 and 34 together with the production capacity data from Table 20. The appropriate emission factor was multiplied by the production capacity nationwide and for each state in which phthalic anhydride plants are located. The total mass emissions from all sources nationwide and for each state were obtained from Reference 51. The percent contributions to the total emissions resulting from phthalic anhydride production were computed using these values. The results are presented in Table 39 for nationwide emissions, and Table 40 for individual state emissions.

5. Affected Population

A measure of the population which is exposed to a high contaminant concentration due to a representative phthalic anhydride plant can be obtained as follows. The values of x for which

$$\frac{\bar{\chi}(x)}{F} = 0.1 \text{ or } 1.0 \qquad (4)$$

are determined by iteration. The value of $\bar{\chi}(x)$, the annual mean ground level concentration, is computed from the equation:[49]

$$\bar{\chi}(x) = \frac{2.03\ Q}{\sigma_z \bar{u} x} \exp\left[-\frac{1}{2}\left(\frac{H}{\sigma_z}\right)^2\right] \qquad (5)$$

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[51] 1972 National Emissions Report. U.S. Environmental Protection Agency. Research Triangle Park. Publication No. EPA-450/2-74-012. June 1974.

Table 39. NATIONWIDE EMISSIONS OF CRITERIA POLUTANTS FROM PHTHALIC ANHYDRIDE INDUSTRY (CONTROLLED EMISSIONS)

Material emitted	Source	Emissions, metric tons/yr	% Contribution
Carbon monoxide	All sources	97.6 x 10^6[a]	100.
	Phthalic anhydride production	608	0.00062
	o-Xylene based	413	0.00042
	Naphthalene based	195	0.00020
Sulfur oxides	All sources	30.2 x 10^6[a]	100.
	Phthalic anhydride production	1,500	0.0050
	o-Xylene based	1,500	0.0050
	Naphthalene based	0	0
Particulates	All sources	18.0 x 10^6[a]	100.
	Phthalic anhydride production	169	0.00094
	o-Xylene based	113	0.00063
	Naphthalene based	56	0.00031
Nitrogen oxides	All sources	22.4 x 10^6[a]	100.
	Phthalic anhydride production	619	0.0028
	o-Xylene based	413	0.0018
	Naphthalene based	206	0.0009
Hydrocarbons[b]	All sources	25.3 x 10^6[a]	100.
	Phthalic anhydride production	1,089	0.0043
	o-Xylene based	865	0.0034
	Naphthalene based	224	0.0009

[a] Data obtained from Reference 51.

[b] Includes all non-methane organic species.

Table 40. EMISSIONS OF CRITERIA POLLUTANTS FROM PHTHALIC ANHYDRIDE INDUSTRY BY STATE (CONTROLLED EMISSIONS)

Material emitted	State	Total emissions,[a] 10^6 metric tons/yr	Emissions from phthalic anhydride plants, metric tons/yr	Phthalic anhydride contribution, %
Carbon monoxide	California	8.25	53	0.0006
	Illinois	6.43	141	0.0022
	Louisiana	5.65	56	0.0010
	New Jersey	2.88	134	0.0047
	Pennsylvania	3.74	142	0.0038
	Texas	6.91	81	0.0012
Sulfur oxides	California	0.39	192	0.0492
	Illinois	2.05	510	0.0249
	Louisiana	0.17	204	0.1200
	New Jersey	0.46	295	0.0641
	Pennsylvania	2.94	0	0.0
	Texas	0.75	295	0.0393
Particulate	California	1.01	14	0.0014
	Illinois	1.15	38	0.0033
	Louisiana	0.38	15	0.0039
	New Jersey	0.15	38	0.0250
	Pennsylvania	1.81	41	0.0023
	Texas	0.55	22	0.0040
Nitrogen oxides	California	1.67	53	0.0032
	Illinois	0.98	141	0.0144
	Louisiana	0.42	56	0.0133
	New Jersey	0.49	137	0.0280
	Pennsylvania	3.02	149	0.0049
	Texas	1.31	81	0.0062
Hydrocarbons[b]	California	2.17	111	0.0051
	Illinois	1.83	295	0.0161
	Louisiana	1.92	118	0.0061
	New Jersey	0.82	231	0.0282
	Pennsylvania	0.89	162	0.0182
	Texas	2.22	170	0.0077

[a] Data obtained from Reference 51.

[b] Includes all non-methane organic species.

where Q = emission rate, g/sec
H = effective emission height, m
x = downwind distance from source, m
$\bar{u}$ = average wind speed (4.5 m/sec)
σ_z = vertical dispersion coefficient, m

For atmospheric stability class C (neutral conditions), σ_z is given by:[52]

$$\sigma_z = 0.113\ x^{0.911} \tag{6}$$

The affected area is then computed as

$$A = \pi(x_2{}^2 - x_1{}^2),\ \text{km}^2 \tag{7}$$

where x_1 and x_2 are the two roots of Equation (4).

The (capacity weighted) mean population density, $\bar{D}_P$, is calculated for each plant type (o-xylene and naphthalene) as follows:

$$\bar{D}_P = \frac{\sum_i C_i D_{P_i}}{\sum_i C_i},\ \text{persons/km}^2 \tag{8}$$

where C_i = production capacity of plant i
D_{P_i} = county population density for plant i

The product $A \cdot \bar{D}_P$ is designated the "affected population."

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[52] Eimutis, E. C., and M. G. Konicek. Derivations of Continuous Functions for the Lateral and Vertical Atmopheric Dispersion Coefficients. Atmospheric Environment. 6:859-863, 1972.

Table 41. AFFECTED POPULATION
(number of persons)

Compound	o-Xylene based plant		Naphthalene based plant	
	No. of persons where $\overline{\chi}/F \geq 1.0$	No. of persons where $\overline{\chi}/F \geq 0.1$	No. of persons where $\overline{\chi}/F \geq 1.0$	No. of persons where $\overline{\chi}/F \geq 0.1$
Sulfur oxides				
Main process incinerator	0	6,700	-[a]	-[a]
Nitrogen oxides				
Main process incinerator	0	5,600	0	870
Total hydrocarbons				
Main process incinerator	0	9,600	0	0
Fugitive emissions	40	500	6	77
Phthalic anhydride				
Main process incinerator	0	19,000	0	4,100
Secondary incinerator	0	3,100	0	460
Transport loading	0	140	0	22
Maleic anhydride				
Main process incinerator	44,000	525,000	0	9,200
Secondary incinerator	0	8,800	0	1,800
Diphenyl oxide				
Fugitive emissions	300	3,400	50	540
Formaldehyde				
Main process incinerator	0	15,000	0	2,300
Naphthoquinone				
Main process incinerator	-[a]	-[a]	0	1,300
Secondary incinerator	-[a]	-[a]	500	7,000
Vanadium oxide catalyst				
Catalyst storage	-[a]	-[a]	40	650

[a] No emissions.

The affected population was computed for each compound and each source for which the severity factor, S, exceeds 0.1. The results are presented in Table 41. The mean population density for O-xylene based plants is 1,667 persons per square kilometer, and for naphthalene based plants it is 261 persons per square kilometer. For $\overline{\chi}/F \geq 0.1$, the total number of persons affected by a representative o-xylene based plant is 525,000 persons, while the total number affected by a representative naphthalene based plant is 9,200 persons. For $\overline{\chi}/F \geq 1.0$, the values are 44,000 persons for an o-xylene based plant and 500 persons for a naphthalene based plant.

6. Growth Factor

In 1973, 4.658×10^5 metric tons of phthalic anhydride was produced in the United States.[53] As discussed in Section VI, production is expected to total 4.99×10^5 metric tons in 1978. Thus, assuming that the same level of control technology exists in 1978 as existed in 1973, the emissions from the phthalic anhydride industry will increase by 7% over that period; i.e.:

$$\frac{\text{Emissions in 1978}}{\text{Emissions in 1973}} = \frac{4.99 \times 10^5}{4.658 \times 10^5} = 1.07$$

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[53] Naphthalene Feedstock Outlook Mixed. Chemical and Engineering News. 52:14-17, July 8, 1974.

SECTION V

CONTROL TECHNOLOGY

A. STATE OF THE ART

At the present time, all phthalic anhydride plants employ pollution control devices to treat the switch-condenser off-gas, which constitutes the greatest potential source of air pollution from phthalic anhydride manufacture. The control devices in use are water scrubbers and/or incinerators, either thermal or catalytic. The large air to feed ratio, particularly in o-xylene based plants, makes the scrubber-incinerator combination more economical than incineration alone due to the large volume of gas that must be handled.

Organic removal efficiencies of up to 98% to 99% in the scrubber and 99.9% in the incinerator are achieved.[38] However, carbon monoxide and sulfur oxides are not controlled and are emitted to the atmosphere via the scrubber vent. Further treatment of the scrubber vent gas (e.g., by a CO boiler or gas adsorption) would be expensive due to the low concentration (approximately 0.6% by weight) of pollutants in this stream. The principal advantage of direct incineration of the switch-condenser off-gas is that it allows the carbon monoxide to be controlled. Control efficiencies of 99.9% can be achieved for this contaminant with an organic conversion efficiency of 96.5%.[13] The sulfur oxides are again vented to the atmosphere, however.

The scrubber and/or incinerator can also be used to control the waste streams from the product purification section of the phthalic anhydride plant. Alternatively, a separate control device may be employed for this purpose. The best control system presently in use employs direct thermal incineration of the switch-condenser off-gas together with a second thermal incinerator that handles the waste streams from the product purification section. Water scrubbers are also used in some plants to treat some of the latter streams.

The dual incineration system provides better overall emissions control than the scrubber-incinerator system or other systems being used for the following reasons:

(1) The removal efficiency for total organics is 96.5% for the dual incineration system being used at two phthalic anhydride plants. The scrubber-incinerator system is capable of achieving 97% removal of total organics in existing commercial plants, but the dual incineration system has a better potential for increased organics removal through increased incineration temperatures in the existing plants. Theoretical calculations indicate that the organics removal efficiency will be 99% when operating at a temperature of approximately 860°C instead of 760°C.[54] The scrubber-incinerator system does not demonstrate this flexibility in existing plants.

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[54] Chi, C. T., and T. W. Hughes. Technical and Economic Evaluation of Phthalic Anhydride Plant Air Pollution Control. Monsanto Research Corporation. Dayton. Preliminary Draft Report. U.S. Environmental Protection Agency, Contract 68-02-1320, Task 25. August 1976.

However, increasing the flame temperature in the dual incineration system by 100°C will increase the NO_x emissions by about 15%. The NO_x source severity at 760°C is 0.14; at 860°C it will be 0.16 (0.14 x 1.15).

(2) Direct thermal incineration of the switch-condenser off-gas removes 99% of the carbon monoxide. The scrubber incinerator system cannot control carbon monoxide emissions since the incineration is performed on the scrubber purge liquid (blowdown) and not on the scrubber vent gas. The carbon monoxide source severities for the dual incineration system and the scrubber-incineration system on an o-xylene based plant are 0.000053 and 0.21, respectively. For a naphthalene based plant, the severities are 0.000021 for dual incineration and 0.084 for the scrubber-incineration combination.

The percent contribution to nationwide carbon monoxide emissions is 0.002% for dual incineration versus 0.047% for the scrubber-incinerator system. The contributions to total carbon monoxide emissions in New Jersey (the largest of the statewide contributions) are 0.0047% for the dual incineration system and 0.43% for the scrubber-incinerator combination.

(3) The use of a secondary (dual) incinerator for control of waste streams from the product purification section of the plant is preferable to use of a secondary scrubber to control these streams. The dual incinerator has a high (99%) control efficiency for organics and does not generate an additional liquid waste stream requiring disposal as does scrubbing.

(4) The use of a secondary incinerator for the product purification waste streams is also superior, from an operating standpoint, to using the main process incinerator for control of these streams. The product purification waste streams vary in flow rate, physical properties, and composition from the switch-condenser off-gas. The secondary incinerator is designed for optimal control of product purification wastes while the main process incinerator is designed for optimal control of the switch-condenser off-gas.

Emissions from o-xylene storage tanks are controlled by the use of conservation vents. Phthalic anhydride storage tanks are controlled by means of condensers or sublimation traps, or by venting to the incinerator. Naphthalene storage tanks can also be controlled by means of conservation vents. In most plants, however, either some or all of the storage tanks are vented directly to the atmosphere.

Cyclones and baghouses are used to control the emission of phthalic anhydride dust from the flaking and bagging operations. In the case of naphthalene based plants, cyclones are also used on the new and spent catalyst storage hopper vents to control the emission of vanadium oxide catalyst dust during catalyst transfer operations.

B. PROCESS MODIFICATIONS

A number of modifications to the basic phthalic anhydride process have been proposed in the recent literature. Since these modifications will potentially have an effect on pollution control methodology with respect to phthalic anhydride production, they are discussed in this section.

1. The Rhone-Progil "Chauney '71" Process

A new process for the production of phthalic anhydride from o-xylene has been developed by Rhone-Progil in France.[55] A 1.5×10^4 metric tons/yr plant has been in operation since 1971 in Aisne, France, and the process has been licensed to Resins, Inc. (Philippines) and to Reposa (Spain). The flow diagram for the new process is very similar to that for the BASF process (Figure 2), with the following differences:

- No sulfur or sulfur dioxide is required in the reactor feed to maintain catalyst activity. Hence, this source of pollution is eliminated.

- The switch-condenser off-gas is controlled by means of a catalytic incinerator without an intermediate scrubber. This control method is economically more attractive here than with the BASF process due to a lower air to o-xylene feed ratio. (Specific figures have not been published.)

- The liquid waste stream from the distillation section is further processed to produce solid pellets, which are disposed of by burning.

It is claimed[55] that the exhaust gases from this process "meet all existing and forecasted regulations."

2. Maleic Anhydride Recovery

The UCB (Brussels, Belgium) process for the recovery of maleic anhydride from the scrubber liquid waste stream is described in Reference 56. A similar process has been developed by BASF.[57] Instead of being sent to the incinerator for disposal, the scrubber liquid purge stream is sent to the continuous maleic anhydride recovery system shown schematically in Figure 9. The recovery process can be divided into three steps: concentration, dehydration, and distillation. The first step removes the organic compounds from the scrubber purge stream in two stages. In the first stage, part of the water is evaporated at a closely controlled temperature to avoid any crystallization of organics. In the second stage, the remaining water is flashed off in an evaporator, leaving a bottom stream of liquid organics. The water removed in both stages, which contains some residual organic material, is condensed and recycled to the scrubber.[a]

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[55] Zimmer, J. C. New Phthalic Anhydride Process. Hydrocarbon Processing. 53:132-134, November 1974.

In the second step, the liquid organic stream is sent to a dehydration unit where the organic acids are thermally dehydrated to the anhydrides. The maleic anhydride and dehydration water are distilled off and separated by a selective condensation process. The water is recycled to the scrubber, while the crude maleic anhydride is sent to the vacuum distillation column for purification (Step 3). The refined maleic anhydride (97.7%) is taken overhead and the bottom stream from the distillation column is recycled to the dehydrator. If maleic anhydride of greater purity is required, a further purification step can be added.

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[a] The recovery of the water is also important because sodium ion-free water must be used in the process. Sodium ions catalyze the polymerization of maleic anhydride, and this reaction can result in an explosion.

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[56] Weyens, E. Recover Maleic Anhydride. Hydrocarbon Processing. 53:132-134, November 1974.

[57] Wirth, F. Recover MA from PA Scrubber Water. Hydrocarbon Processing. 54:107-108, August 1975.

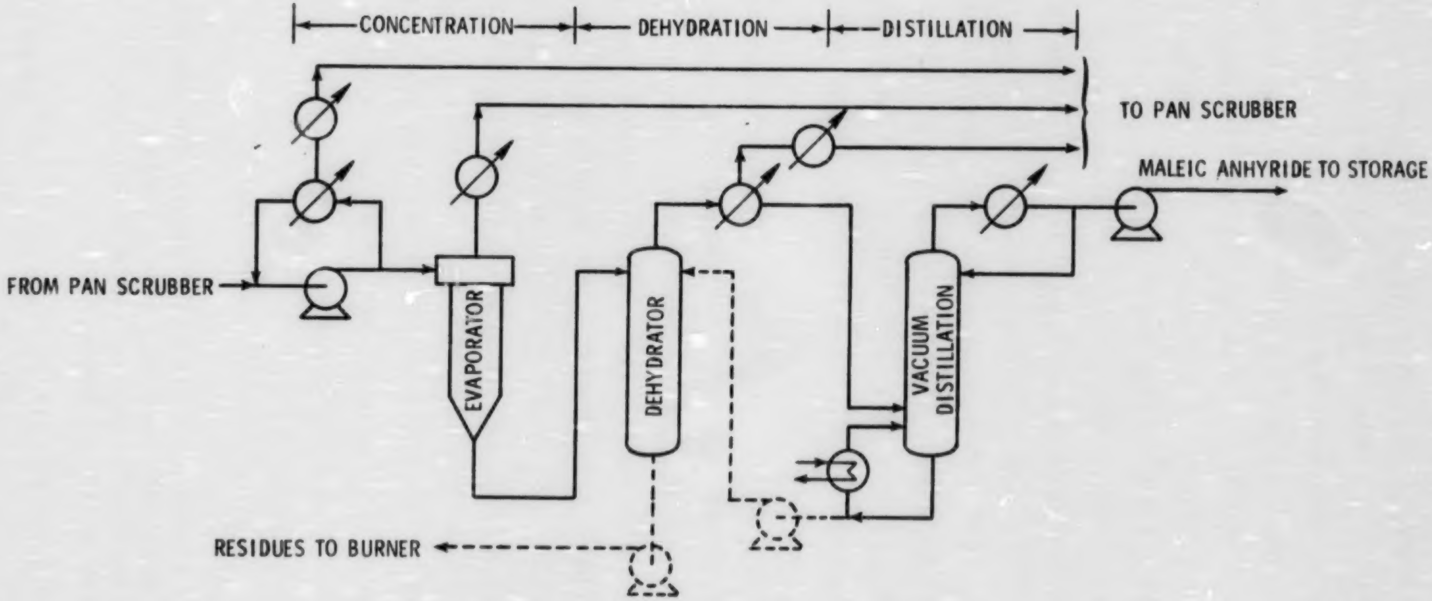
CONCENTRATION
DEHYDRATION
DISTILLATION
TO PAN SCRUBBER
MALEIC ANHYRIDE TO STORAGE
FROM PAN SCRUBBER
EVAPORATOR
DEHYDRATOR
VACUUM DISTILLATION
RESIDUES TO BURNER

Figure 9. Maleic anhydride recovery process[56]

The major components in the liquid waste stream from the dehydrator are phthalic anhydride, benzoic acid, citraconic anhydride, and maleic anhydride. This stream can be disposed of in a conventional burner. Hence, a phthalic anhydride plant incorporating this modification does not require an incinerator for waste disposal.

3. Direct Production of Phthalates

The single largest use of phthalic anhydride is in the production of ortho-phthalates, which are used as plasticizers. Phthalates are manufactured by reacting phthalic anhydride with the desired alcohol in the presence of sulfuric acid, which catalyzes the reaction. Wu and Maa[58] have suggested a modification of the phthalic anhydride process, by which the phthalate, rather than phthalic anhydride, is produced. A schematic flow diagram of the proposed process is shown in Figure 10. The reactor gases (stream 5), instead of being sent to switch-condensers, are fed to an absorption tower where they are contacted with an alcohol-sulfuric acid mixture (stream 6). The phthalic anhydride is absorbed in the alcohol and reacts to form the monoester. Thus, separation of phthalic anhydride from the gas mixture and esterification to monoester are carried out in a single step. The monoester-alcohol-sulfuric acid mixture (stream 8) is sent to a fractionation tower where the reaction proceeds further to form the diester. The phthalate is taken off as the bottom stream (stream 9) from the fractionation tower, while the overhead stream (stream 10) is condensed and sent to a separator where the water formed in the esterification reaction is removed. The

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[58] Wu, W. H., and J. R. Maa. Make Phthalates Direct. Hydrocarbon Processing. 53:117-118, April 1974.

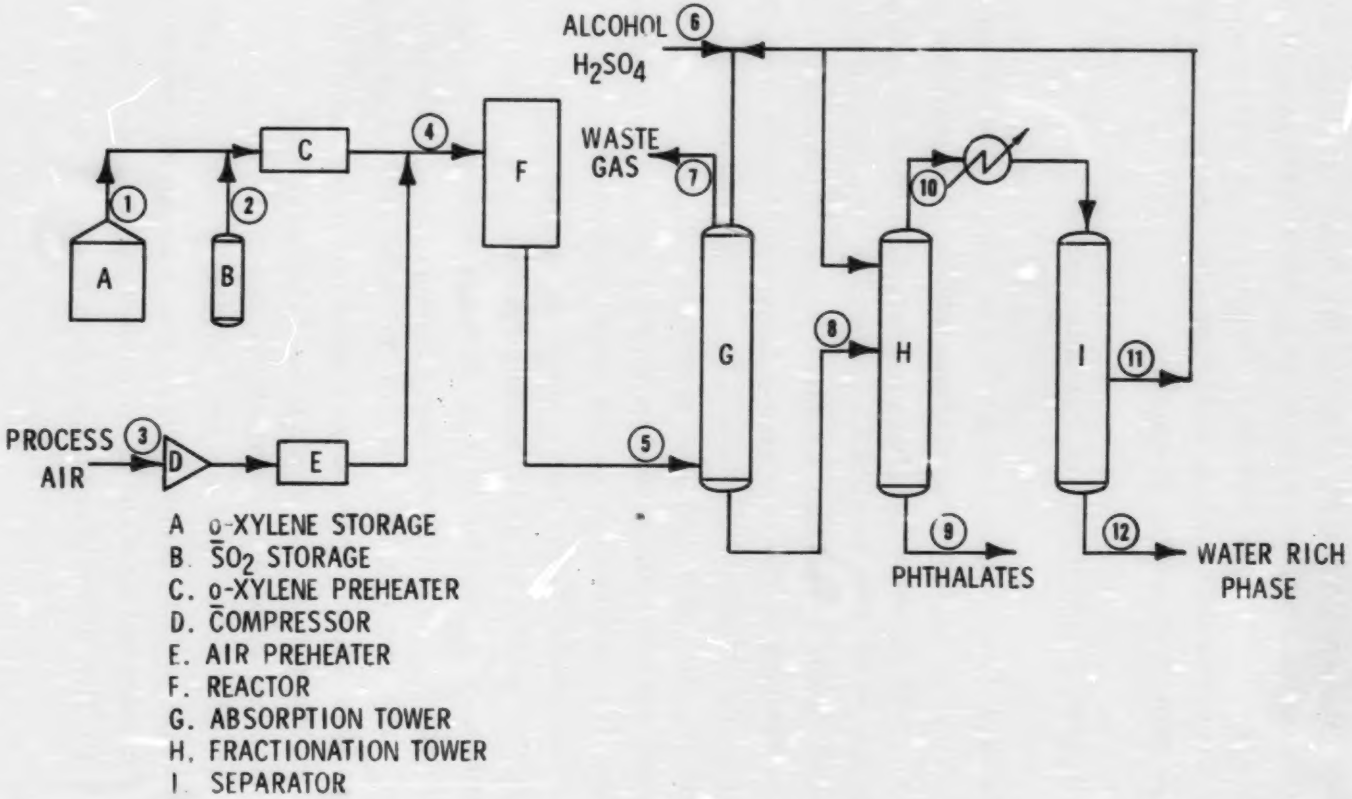
ALCOHOL
H$_2$SO$_4$
WASTE GAS
PROCESS AIR
PHTHALATES
WATER RICH PHASE
A
B
C
D
E
F
G
H
I
①
②
③
④
⑤
⑥
⑦
⑧
⑨
⑩
⑪
⑫
A o-XYLENE STORAGE
B. SO$_2$ STORAGE
C. o-XYLENE PREHEATER
D. COMPRESSOR
E. AIR PREHEATER
F. REACTOR
G. ABSORPTION TOWER
H. FRACTIONATION TOWER
I. SEPARATOR

Figure 10. Flow diagram for direct production of phthalates[58]

organic-rich phase (stream 11) from the separator is recycled to the absorption and fractionation towers.

The waste gas stream from the absorption tower (stream 7) is expected to have a composition similar to the switch-condenser off-gas in the standard phthalic anhydride process. Hence, scrubbing and/or incineration would be required as control measures for this stream. The principal advantage of the modified process, from the standpoint of air pollution control, is that the emissions from the product purification section of the standard phthalic anhydride plant would be eliminated. Emissions of heat-transfer fluid from the switch-condenser heat-transfer circuits would also be eliminated, as well as phthalic anhydride emissions from the flaking and bagging operations. Phthalic anhydride emissions from storage tanks and the transport loading facility vent would be replaced by phthalate emissions. The other waste stream from the modified process is the water-rich phase (stream 12) from the separator. This stream is expected to contain, as contaminants, alcohol, sulfuric acid, phthalic acid, maleic acid, benzoic acid, phthalate and other organics. Hence, this stream presents a serious water pollution control problem.

4. Alternate Feedstocks

Phthalic anhydride processes based on feed materials other than o-xylene and naphthalene are possible and may become important in the future should supplies of the latter materials become scarce. Two alternate raw materials that have been used are methyl naphthalene, which must be demethylated prior to use, and acenaphthlene.[59] Both of these compounds are obtained from coal tar. In fact, coal tar contains more methyl naphthalenes than naphthalene.

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[59] Austin, G. T. Industrially Significant Organic Chemicals, Part 8. Chemical Engineering, 24:107, July 22, 1974.

SECTION VI

GROWTH AND NATURE OF THE INDUSTRY

A. PRESENT TECHNOLOGY

Phthalic anhydride is currently produced in the United States from o-xylene via the fixed-bed process and from naphthalene via the fluid-bed process. The BASF process is the most recent and most widely used fixed-bed process, while the Badger-Sherwin-Williams process is the dominant fluid-bed process. In recent years, o-xylene has become the preferred feedstock due to its lower unit product cost, and all new plants built since 1968 use o-xylene. This trend is further reflected in the fact that since 1968, 10 naphthalene based plants in the U.S. have been shut down and naphthalene based capacity has declined from 2.39×10^5 metric tons/yr in 1968 to 1.5×10^5 metric tons/yr in 1975.[1,3,4] (However, a 2.27×10^4 metric tons/yr expansion of the U.S. Steel naphthalene based plant is scheduled for start up in 1975.[4]) This trend could be reversed in the future if rising petroleum prices should result in a more favorable price for coal-tar naphthalene than for o-xylene. Since the fixed-bed plants are capable of operating with either o-xylene or naphthalene, a change of feedstock could be made both quickly and easily.

B. EMERGING TECHNOLOGY

Two significant improvements in the fixed-bed o-xylene based process have been made by Rhone-Progil.[55] First, in the Rhone-Progil process sulfur dioxide is not required in the reactor feed stream to maintain catalyst activity. Hence, this source of air pollution is eliminated. Second, a lower air to xylene feed ratio has been achieved (although a specific figure has not been published), thus reducing the volume of waste gas that must be treated. This reduction in the volume of waste gas improves the economics of treatment by direct incineration, as opposed to treatment by a scrubber-incinerator combination. Direct incineration has the advantage of controlling the emission of the carbon monoxide that is present in the waste gas stream.

Other recent innovations in phthalic anhydride production involve the recovery of maleic anhydride[56] and benzoic acid[55] as by-products from the waste gas stream. The production cost of maleic anhydride by the UCB recovery process[56] is less than the raw material cost alone for the conventional process using benzene. In addition, the cost of process equipment is less than for a benzene based plant of the same capacity. With increasing costs for petrochemicals, it is expected that by-product recovery from phthalic anhydride production will become even more economically attractive in the future.

C. MARKETING STRENGTHS AND WEAKNESSES

Figure 11 shows schematically the usage of phthalic anhydride in the United States.[60] Each of the major product categories is discussed below.

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[60] Chemical Origins and Markets, 4th Edition. Menlo Park, Stanford Research Institute, Chemical Information Services, 1967. 99 p.

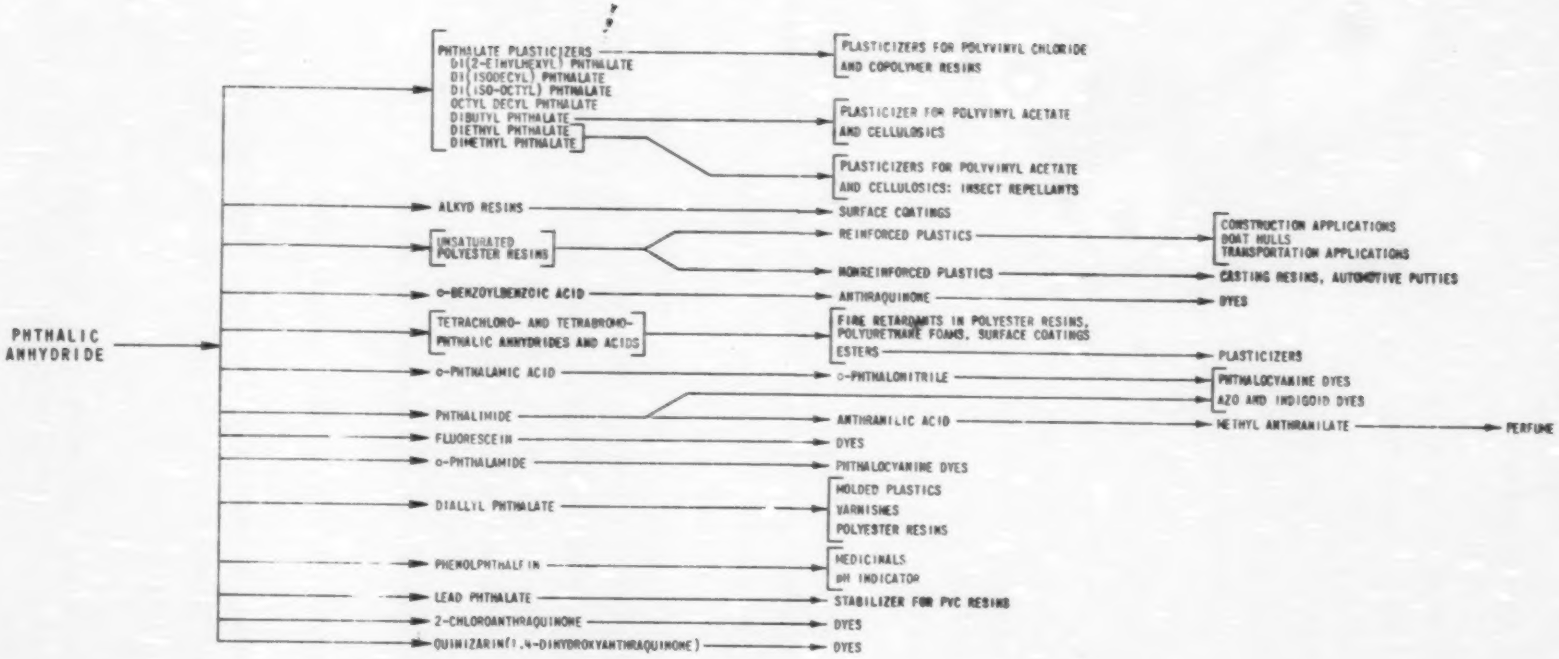
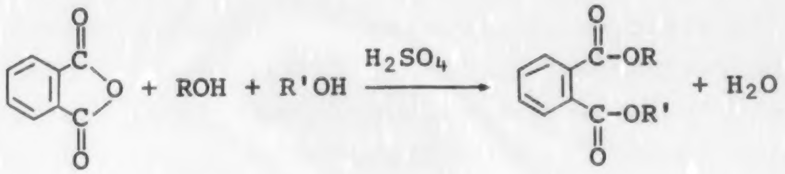

PHTHALIC ANHYDRIDE
PHTHALATE PLASTICIZERS
DI(2-ETHYLHEXYL) PHTHALATE
DI(ISODECYL) PHTHALATE
DI(ISO-OCTYL) PHTHALATE
OCTYL DECYL PHTHALATE
DIBUTYL PHTHALATE
DIETHYL PHTHALATE
DIMETHYL PHTHALATE
PLASTICIZERS FOR POLYVINYL CHLORIDE AND COPOLYMER RESINS
PLASTICIZER FOR POLYVINYL ACETATE AND CELLULOSICS
PLASTICIZERS FOR POLYVINYL ACETATE AND CELLULOSICS: INSECT REPELLANTS
ALKYD RESINS
SURFACE COATINGS
UNSATURATED POLYESTER RESINS
REINFORCED PLASTICS
CONSTRUCTION APPLICATIONS
BOAT HULLS
TRANSPORTATION APPLICATIONS
NONREINFORCED PLASTICS
CASTING RESINS, AUTOMOTIVE PUTTIES
o-BENZOYLBENZOIC ACID
ANTHRAQUINONE
DYES
TETRACHLORO- AND TETRABROMO-PHTHALIC ANHYDRIDES AND ACIDS
FIRE RETARDANTS IN POLYESTER RESINS, POLYURETHANE FOAMS, SURFACE COATINGS
ESTERS
PLASTICIZERS
o-PHTHALAMIC ACID
o-PHTHALONITRILE
PHTHALOCYANINE DYES
AZO AND INDIGOID DYES
PHTHALIMIDE
ANTHRANILIC ACID
METHYL ANTHRANILATE
PERFUME
FLUORESCEIN
DYES
o-PHTHALAMIDE
PHTHALOCYANINE DYES
DIALLYL PHTHALATE
MOLDED PLASTICS
VARNISHES
POLYESTER RESINS
PHENOLPHTHALEIN
MEDICINALS
pH INDICATOR
LEAD PHTHALATE
STABILIZER FOR PVC RESINS
2-CHLOROANTHRAQUINONE
DYES
QUINIZARIN(1,4-DIHYDROXYANTHRAQUINONE)
DYES

Figure 11. Uses of phthalic anhydride[60]

The largest single use of phthalic anhydride is in the manufacture of plasticizers, which accounts for 50% of the phthalic anhydride produced in the U.S.[3] Plasticizers are diphthalates produced by the esterification reaction of two moles of alcohol with one mole of phthalic anhydride in the presence of sulfuric acid, which catalyzes the reaction.



The major phthalic anhydride plasticizers, with their percentages of total phthalic plasticizer production, are:[1]

di(2-ethylhexyl)phthalate (40%)

di(isodecyl)phthalate (15%)

di(iso-octyl)phthalate (9%)

n-octyl-n-decyl phthalate (6%)

About 87% of these products are used to impart low-temperature flexibility, resilience, high impact strength, and good electrical properties to polyvinyl chloride polymers and copolymers (with vinyl acetate). Hence, their future growth is tied directly to that of non-rigid PVC.

Raw material shortages, the slump in the automobile industry, and concern over the health hazards of vinyl chloride monomer could seriously affect the growth of non-rigid PVC. For example, new legislation restricting worker exposure to vinyl chloride monomer may curtail output and force much higher resin prices.[61] In fact, production for the first quarter of 1975 was down nearly 40% compared to the same period in 1974.[4] In spite of these concerns, however, the industry is planning at least a one-third increase in PVC resin capacity by the end of 1976.[62]

The above caveats notwithstanding, overall plasticizer production is expected to increase at an average annual rate of 5% in the period 1975 to 1980. Phthalate ester plasticizers will ikely increase at a slightly lower level due to an increasing demand for more flame-retardant vinyls, which will result in a greater use of phosphate plasticizers. In addition, some competition is expected from specialty plasticizers such as the trimellitates, the adipates, and the sebacates, in applications where improved properties are important. Historically, phthalate ester plasticizers experienced an average growth rate of 9% in the period 1963 to 1973.[63]

The second largest use of phthalic anhydride is in the manufacture of unsaturated polyester resins, which accounts for 24% of domestic phthalic anhydride production.[3] Unsaturated polyesters are made from unsaturated organic acids (as their anhydrides) and glycols, and are crosslinked with monomers such as styrene, vinyltoluene, and diallyl phthalate. A typical reaction involving maleic and phthalic anhydrides is:

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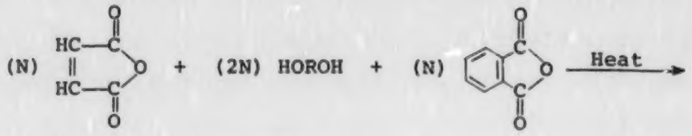
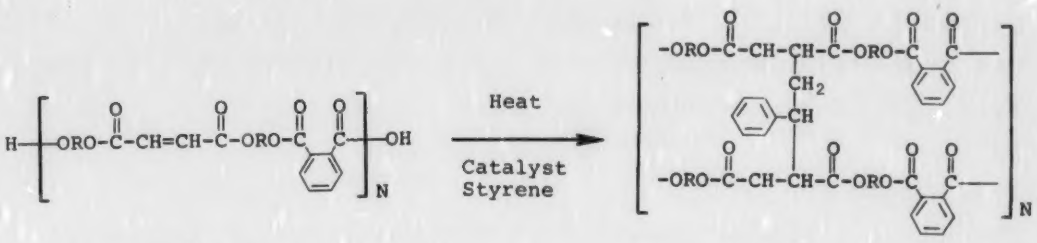
[61] Edwards, P. Chemicals '75/Aliphatics. Chemical Marketing Reporter. 207:40-42, January 6, 1975.

[62] Burke, D. P. Forecast '75 Riding it Out. Chemical Week. 116:17-24, January 8, 1975.

[63] Synthetic Organic Chemicals, U.S. Production and Sales. U.S. International Trade Commission (formerly U.S. Tariff Commission). Washington. 1963-1974.



Maleic anhydride Glycol Phthalic anhydride



Prepolymer

Unsaturated polyester resin

In 1973, 78% of unsaturated polyester resins were used for the production of glass fiber reinforced plastics (FRP) and the remainder for non-reinforced applications.[64]

The average annual growth of unsaturated polyester resin production from 1963 to 1973 was 15%.[65] After a slight decline in 1970, growth in the 1971-1973 period averaged 22%.[65,66] These large increases in polyester resin consumption were the result of a large increase in the pleasure boat business, the large-scale use of synthetic marble and FRP tub/shower units in construction, and the first large-scale applications of low profile, low shrink resins in the transportation and equipment markets.

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[64] 1972 Annual Statistical Report. The Society of the Plastics Industry. New York. November 16, 1973.

[65] Anderson, E. V. Growth Slows in Top 50 Chemicals' Output. Chemical and Engineering News. 52:10-13, May 6, 1974.

The years 1973 and 1974, especially the latter, were characterized by widespread shortages of raw materials, including styrene, maleic anhydride, and most glycols. As of late 1974, raw material availability was generally adequate, although some glycols were still in short supply. As a result of the severe raw material shortages in the first nine months of 1974, reported unsaturated polyester resin production for this period was down by 10% compared to the same period in 1973.[66] Production for the first quarter of 1975 was down 24% compared to the first quarter of 1974.[4] However, growth is expected to resume after the first half of 1975.

The average annual growth rate for unsaturated polyester resins is expected to be 11% to 13% in the period 1974 to 1979. This rate of growth will result in an increase in production from an estimated 3.85×10^5 to 4.4×10^5 metric tons in 1974 to 6.6×10^5 to 8.21×10^5 metric tons in 1979. The demand for phthalic anhydride in this area is expected to grow at a level somewhat below that of total unsaturated polyester resin production. This is due to the substitution (some of which is believed to be permanent) of isophthalic resins for some phthalic-based resins caused by the recent raw materials shortage.

The third major outlet for phthalic anhydride is the production of alkyd resins, which accounts for 19% of domestic phthalic anhydride production.[3] Alkyd resins are a type of polyester resin, being the reaction product of a polybasic acid and a polyol. Alkyds, however, contain an unsaturated monocarboxylic acid, such as those from the drying oils, as a modifying agent. Thus, after coating on a surface, the alkyd resin can undergo further oxidative polymerization like a drying oil to yield a very tough, elastic, weather-resistant film. These synthetic enamels have been used extensively for the finishing of automobiles and household appliances.

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[66] Anderson, E. V. Recession Stifles Output of Top 50 Chemicals. Chemical and Engineering News. 53:30-33, May 5, 1975.

Until 1961, alkyd resin manufacture was the largest single user of phthalic anhydride. The rapid rise in plasticizer demand and, later, in unsaturated polyester resins, combined with the slow growth of alkyd resins (due primarily to competition from other surface coating resins), resulted in alkyds dropping to third on the list of phthalic anhydride consumers. Phthalic anhydride consumption for alkyd resin manufacture has remained nearly static in the period 1967 to 1974 (9.34×10^4 metric tons in 1967 versus 8.89×10^4 metric tons in 1974).[63]

Total alkyd surface coatings consumption is expected to decline at an average annual rate of -5% to -1% in the period 1975-1978, mostly as the result of increased competition from other coating systems and stricter anti-pollution laws governing the use of solvent-based paints.

Exports and various miscellaneous products account for 7% of the phthalic anhydride produced in the U.S.[3] Included in this category are anthraquinone and its derivatives (intermediates for the synthesis of anthraquinone dyes), lead phthalate (a PVC stabilizer), tetrachloro- and tetrabromophthalic anhydride (fire retardants in polyester resins), diallyl phthalate (a crosslinking agent for polyesters), dibutyl phthalate and phthalonitrile (insecticides), phenolphthalein (a pH indicator and laxative), phthalein and xanthene dyes, phthalimide (used in various organic syntheses and in the manufacture of perfume and indigo dye), and eosin (tetrabromofluorescein) inks and dyes.

Exports have exhibited a sharp increase during the past four years, as is shown below:[4,63]

Year	Phthalic anhydride exports, 10^3 metric tons
1971	3.48
1972	6.26
1973	10.08
1974	15.42

During the first quarter of 1975, however, exports ran at an annual rate of only 1.1 x 10^3 metric tons. The reason is that foreign phthalic prices had dropped below the domestic price.[4]

Domestic phthalic anhydride production increased at an average annual rate of 8.4% during the period 1963 to 1973.[3] In 1974, production totaled 4.692 x 10^5 metric tons. During the first quarter of 1975, however, production totaled only 5.62 x 10^4 metric tons.[4] This corresponds to an annual rate of 2.248 x 10^5 metric tons, which is less than half the nominal plant capacity in the U.S. The sharp drop in phthalic production reflects the declines in phthalic's major markets, polyvinyl chloride and unsaturated polyester resins.

Phthalic production is expected to recover in the second half of 1975 to reach a total output of approximately 3.18 x 10^5 metric tons for the year. Annual production is projected to reach 4.99 x 10^5 metric tons in 1978 and 6.35 x 10^5 metric tons in 1980.[4]

SECTION VII

APPENDIXES

A. Storage Tank Calculations

B. Rationale for Not Considering All Species Listed in Table 21

APPENDIX A

STORAGE TANK CALCULATIONS

The procedure for calculating the emissions from storage tanks is outlined in this section. The equations given below were derived in References 39-43.

Step 1. Calculate the equivalent gasoline breathing loss:

$$L_y = \frac{24}{1000}\left(\frac{P}{14.7-P}\right)^{0.68} D^{1.73}(H')^{0.51}\ (\Delta T)^{0.50}\ F_pC \qquad \text{(A-1)}$$

where L_y = equivalent gasoline breathing loss, bbl/yr

P = vapor pressure of material stored at bulk temperature, psia

D = tank diameter, ft

H' = average tank outage, ft

ΔT = average daily ambient temperature change, °F

F_p = paint factor

C = diameter factor

The bulk temperatures of the material stored were taken to be 200°F for naphthalene tanks, 300°F for phthalic anhydride tanks, and 74°F for o-xylene tanks. The latter temperature was obtained by adding 5°F to the ambient temperature, as recommended in References 39-43 for tanks held at ambient temperature. The ambient temperature was assumed to be 69°F, the national mean ambient temperature.

Tank diameters were computed by assuming a height of 50 ft for all tanks. The average tank outage, i.e., freeboard, was taken as one-half the tank height, or 25 ft.

The average daily ambient temperature change, ΔT, was taken as 20°F, which is the national average value. The paint factor, F_p, was assumed equal to unity, the value for white paint in good condition. This factor can be as high as 14.6 for gray surfaces. The diameter factor, C, is equal to unity for tanks 30 ft or larger in diameter. For smaller tanks, the value is obtained from a graph given in Reference 41, and is between 0.25 and 1.0.

Step 2. Calculate the equivalent gasoline working loss:

$$F_g = \left(\frac{3}{10{,}000}\right) PVNK_T \qquad \text{(A-2)}$$

where F_g = equivalent gasoline working loss, bbl/yr
V = tank capacity, bbl
N = number of turnovers per year
K_T = turnover factor = 1.0 for $N \le 36$
$= \frac{180 + N}{6N}$ for $N > 36$

Step 3. Compute total equivalent gasoline loss, L_g:

$$L_g = L_y + F_g \qquad \text{(A-3)}$$

Step 4. Compute petrochemical losses:

$$L = 0.08 \left(\frac{M}{W}\right) L_g \qquad \text{(A-4)}$$

where L = total petrochemical loss, bbl/yr
M = molecular weight of chemical stored
W = liquid density of chemical stored, lb/gal

Step 5. Calculate emission factor:

$$L_1 = L\ (42)(W) \qquad \text{(A-5)}$$

$$E' = \frac{L_1}{Cap} \qquad \text{(A-6)}$$

$$E = \frac{E'}{2} \qquad \text{(A-7)}$$

where L_1 = petrochemical loss, lb/yr

Cap = production capacity, ton/yr

E' = emission factor, lb/ton

E = emission factor, g/kg

The necessary input data for the above calculations are tabulated in Tables A-1 and A-2, while the results are summarized in Tables A-3 and A-4. The tank numbers in these tables correspond to those in Tables 7 and 14 for o-xylene and naphthalene based plants, respectively.

Table A-1. STORAGE TANK INPUT DATA FOR *o*-XYLENE BASED PLANT

Tank number	1	2	3 & 4	5 & 6	7	8
Input data						
Average ambient temp., °F	69	69	69	69	69	69
Average ambient temp. change, °F	20	20	20	20	20	20
Material molecular weight	106	106	148	148	148	148
Liquid density, lb/gal	7.37	7.37	8.35	8.35	8.35	8.35
Vapor pressure at bulk temp., psia	0.194	0.194	0.33	0.33	0.33	0.33
Bulk temp., °F	74	74	300	300	300	300
Tank diameter, ft	17.3	54.8	17.9	17.5	18.5	26.1
Tank outage, ft	25	25	25	25	25	25
Paint factor	1.0	1.0	1.0	1.0	1.0	1.0
Diameter factor	0.81	1.0	0.83	0.82	0.84	0.98
Turnover factor	0.297	1.0	0.63	0.58	0.85	0.85
No. turnovers per year	230	23	65	72	44	44
Tank capacity, bbl	2,070	21,000	2,260	2,140	2,380	4,760

Table A-2. STORAGE TANK INPUT DATA FOR NAPHTHALENE BASED PLANT

Tank number	1	2	3	4	5	6 & 7	8	9
Input data								
Average ambient temp., °F	69	69	69	69	69	69	69	69
Average ambient temp. change, °F	20	20	20	20	20	20	20	20
Material molecular weight	128	128	128	148	148	148	148	148
Liquid density, lb/gal	8.0	8.0	8.0	8.35	8.35	8.35	8.35	8.35
Vapor pressure at bulk temp., psia	0.31	0.31	0.31	0.33	0.33	0.33	0.33	0.33
Bulk temp., °F	200	200	200	300	300	300	300	300
Tank diameter, ft	58.4	58.4	41.3	17.3	37.0	12.8	22.6	22.6
Tank outage, ft	25	25	25	25	25	25	25	25
Paint factor	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Diameter factor	1.0	1.0	1.0	0.81	1.0	0.65	0.93	0.93
Turnover factor	1.0	1.0	1.0	0.37	1.0	0.40	1.0	0.92
No. turnovers per year	1	13	26	148	2	130	2	40
Tank capacity, bbl	23,810	23,180	11,905	2,095	9,524	1,143	3,571	3,571

Table A-3. STORAGE TANK CALCULATION SUMMARY FOR o-XYLENE BASED PLANT

Tank No.	Material stored	Capacity, gal	Losses		Emission factor, g/kg
			gal/yr	lb/yr	
1	o-Xylene	87,000	546	4,027	0.031
2	o-Xylene	880,000	2,770	20,417	0.157
3	Crude product	95,000	858	7,165	0.055
4	Crude product	95,000	858	7,165	0.055
5	Phthalic anhydride	90,000	836	6,977	0.054
6	Phthalic anhydride	90,000	836	6,977	0.054
7	Phthalic anhydride	100,000	872	7,282	0.056
8	Phthalic anhydride	200,000	1,747	14,584	0.112

Table A-4. STORAGE TANK CALCULATION SUMMARY FOR NAPHTHALENE BASED PLANT

Tank No.	Material stored	Capacity, gal	Losses		Emission factor, g/kg
			gal/yr	lb/yr	
1	Naphthalene	1,000,000	2,582	20,658	0.165
2	Naphthalene	1,000,000	3,970	31,759	0.254
3	Naphthalene	500,000	2,899	23,194	0.186
4	Crude product	88,000	953	7,954	0.064
5	Crude product	400,000	1,422	11,872	0.095
6	Phthalic anhydride	48,000	490	4,090	0.033
7	Phthalic anhydride	48,000	490	4,090	0.033
8	Phthalic anhydride	150,000	577	4,819	0.039
9	Phthalic anhydride	150,000	1,310	10,937	0.088

APPENDIX B

RATIONALE FOR NOT CONSIDERING ALL SPECIES LISTED IN TABLE 21

A number of the possible reaction products listed in Table 21 were not studied explicitly in this work since they are emitted in, at most, trace amounts. The compounds are not emitted in greater than trace amounts for the following reasons:

- They are not formed in greater than trace amounts, due either to unfavorable conditions in a commercial reactor, or to the fact that they are reaction products of feedstock impurities which are themselves present in small amounts.
- They are too reactive to be stable under the process conditions.

An exception is citraconic anhydride, which may be emitted in greater than trace amounts. However, it is undoubtedly included in the reported data as maleic anhydride, since the two are chemically very similar. This is not considered to be a drawback because it is reasonable to assign citraconic anhydride the same TLV as that of maleic anhydride (in lieu of other information) and to treat the two together for the purpose of pollution control.

Each of the compounds listed in Table 21 but not explicitly included in the study is listed in Table B-1, together with the reason for its exclusion.

Table B-1. COMPOUNDS NOT INCLUDED IN STUDY

Compound	Reason for exclusion
o-Methylbenzyl alcohol	Reactive intermediate
o-Toluic acid	Reactive intermediate
p-Toluic acid	Precursor is feed impurity
Toluene	Reactive; formation not favored under commercial reactor conditions
o-Hydroxymethylbenzoic acid	Reactive intermediate
Citraconic anhydride	Reported as maleic anhydride
Phthalide	Reactive intermediate
Phthalaldehydic acid	Reactive intermediate
Phthalic acid	Emitted as phthalic anhydride
Terephthalic acid	Precursor is feed impurity
p-Benzoquinone	Precursor is feed impurity
Isophthalic acid	Precursor is feed impurity
o'-Carboxylphenyl-o-methylphenyl acetate	Formation not favored under commercial reactor conditions; would be decomposed by incineration
o'-Methylphenyl-o-methylphenyl acetate	
bis(o-Methylphenyl)methyl ether	
1,2-bis(o-Methylphenyl)ethane	

As a further justification for not considering the above compounds, upper limits were estimated for the source severity due to these compounds. All of the above compounds are included in the category "miscellaneous organics" listed in Tables 18 and 19. (See also Table 33, footnote l, and Table 34, footnote p.) For the purpose of this calculation, it is assumed that the miscellaneous organics in the reactor product stream are partitioned between the crude product and switch-condenser off-gas in the same ratio as phthalic anhydride. Using the data in Table 18 for o-xylene based plants, this procedure yields 33.3 kg/hr miscellaneous organics in the crude product stream, and 0.8 kg/hr in the switch-condenser off-gas. The former amount is assumed to be removed during product purification and sent to the secondary incinerator. The latter amount is sent to the main process incinerator. Removal efficiencies of 96.5% in the main process incinerator and 99% in the secondary incinerator are assumed. These are the values for total organics obtained from Reference 13. The resulting emission rates are 0.028 kg/hr from the main process incinerator and 0.333 kg/hr from the secondary incinerator. The corresponding source severities are:

$$S = \frac{1.15 \times 10^{-5}}{TLV} \text{ for main process incinerator}$$

$$S = \frac{5.5 \times 10^{-4}}{TLV} \text{ for secondary incinerator}$$

Assuming an average TLV for the miscellaneous organics of 0.001 g/m^3 (equivalent to maleic anhydride), the source severities are 0.01 for the main process incinerator and 0.55 for the secondary incinerator.

A TLV of 0.001 g/m^3 represents a very stringent assumption, since maleic anhydride has the lowest TLV of the major species which are emitted. If the TLV for phthalic anhydride (0.006 g/m^3) is used in the calculation, the severity for the secondary incinerator is less than 0.1. In addition, the estimated severities are for the total of all species included in the miscellaneous organics category. The severity for any individual compound should be much smaller.

A similar calculation based on the data in Table 19 for a naphthalene based plant results in the following source severities for miscellaneous organics:

$$S = \frac{1.03 \times 10^{-5}}{TLV} \text{ for main process incinerator}$$

$$S = \frac{6.08 \times 10^{-4}}{TLV} \text{ for secondary incinerator}$$

Assuming a TLV of 0.001 g/m^3 yields source severities of 0.01 for the main process incinerator and 0.61 for the secondary incinerator.

SECTION VIII

GLOSSARY OF TERMS

ATMOSPHERIC STABILITY CLASS - Class used to designate degree of turbulent mixing in the atmosphere.

BADGER-SHERWIN-WILLIAMS PROCESS - Fluid-bed process developed by Sherwin-Williams Co. and the Badger Company for the oxidation of naphthalene to phthalic anhydride.

BASF PROCESS - Fixed-bed process developed by Badische Anilin and Soda Fabrik for the oxidation of *o*-xylene to phthalic anhydride.

CRITERIA POLLUTANT - Emission species for which an ambient air quality standard has been established.

EMISSION FACTOR - Weight of material emitted to the atmosphere per unit weight of phthalic anhydride produced.

FLAKER - Device which solidifies liquid phthalic anhydride in the form of flakes.

MAIN PROCESS INCINERATOR - Incinerator which burns the off-gas from the switch condenser.

NON-CRITERIA POLLUTANT - Emission species for which no ambient air quality standard has been established.

PARTIAL CONDENSER - Condenser used to condense phthalic anhydride as a liquid in the fluid-bed process.

SECONDARY INCINERATOR - Incinerator which burns the waste streams from the product purification section of the phthalic anhydride plant.

SWITCH CONDENSER - Condenser used to condense phthalic anhydride as a solid.

TANK OUTAGE - Distance from liquid surface to top of storage tank.

SECTION IX

CONVERSION FACTORS AND METRIC PREFIXES[67]

CONVERSION FACTORS

To convert from	to	Multiply by
degree Celsius	degree Fahrenheit	$t_F^\circ = 1.8\ t_C^\circ + 32$
joule (J)	British thermal unit	9.479×10^{-4}
kelvin	degree Celsius	$t_C^\circ = t_K^\circ - 273.15$
kilogram (kg)	pound-mass (lb mass avoirdupois)	2.204
kilogram (kg)	ton (short, 2,000 lb mass)	1.102×10^{-3}
meter (m)	angstrom	1.000×10^{10}
meter (m)	foot	3.281
meter (m)	micron	1.000×10^{6}
meter (m)	mile	6.215×10^{-4}
meter^3 (m^3)	barrels (42 gal)	6.293
meter^3 (m^3)	gallon (U.S. liquid)	2.642×10^{2}
pascal (Pa)	$\text{pound-force/inch}^2$ (psi)	1.450×10^{-4}

PREFIXES

Prefix	Symbol	Multiplication factor	Example
mega	M	10^6	5 MJ = 5×10^6 joules
kilo	k	10^3	5 kg = 5×10^3 grams
milli	m	10^{-3}	5 mm = 5×10^{-3} meter
micro	μ	10^{-6}	5 μm = 5×10^{-6} meter
nano	n	10^{-9}	5 nm = 5×10^{-9} meter

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[67] Metric Practice Guide. American Society for Testing and Materials. Philadelphia. ASTM Designation: E 380-74. November 1974. 34 p.

SECTION X

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